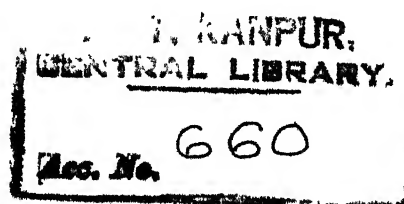
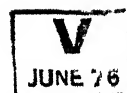


REMOVAL OF PHOSPHATE BY ALUM COAGULATION FROM PURE SOLUTION AND WASTE WATER

A THESIS

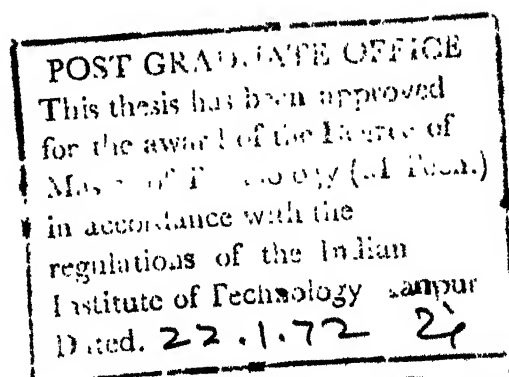
Submitted in Partial Fulfilment of the requirements
for the Degree of

MASTER OF TECHNOLOGY



By

NAKUL CHANDRA SADHUKHAN



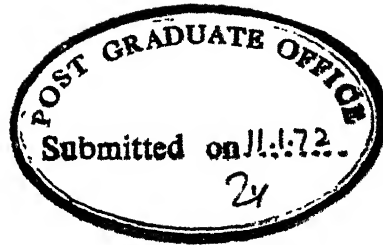
to the

DEPARTMENT OF CIVIL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

January, 1972

Thesis
628.5
Sa 15

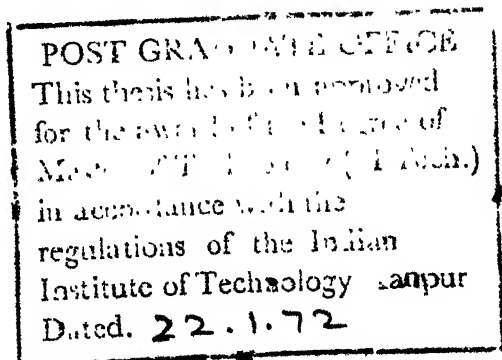


CERTIFICATE

This is to certify that the present work
has been carried out by Sri Mahesh Chandra Sahu
under my supervision and the work has not been
submitted elsewhere for a degree.

B. C. Raymahashay

DR. B.C. RAYMAHASHAY
Assistant Professor
Department of Civil Engineering
Indian Institute of Technology
KANPUR



ACKNOWLEDGEMENT

I express my deep gratitude to Dr. B.C. Raymahashay for his able guidance and constant encouragement during the course of this study.

I also wish to offer my cordial thanks to Dr. G.D. Agrawal, Dr. A.V.S. Prabhakara Rao and Dr. Malay Chowdhury for their valuable suggestions and criticisms from time to time.

Finally my deep appreciation and sincere thanks go to Mr. C. Venkobachar, H.S. Maiti, A.K. Mandal and all my friends of Sanitary Engineering Department who never hesitated to extend their hands whenever I sought their help.

NAKUL CHANDRA SADIUKHAN

CONTENTS

	Page
NOTATIONS	vi
LIST OF TABLES	vi
LIST OF FIGURES	vii
ABSTRACT	ix
CHAPTER - I : INTRODUCTION	1
CHAPTER - II : LITERATURE REVIEW AND OBJECTIVE OF PRESENT WORK	4
2.1 Forms of Phosphorous in Waste Water	4
2.2 Level to Which the Phospho- rous should be Removed	7
2.3 Removal Methods	8
2.4 Mechanism of Removal	12
2.5 Objective	14
CHAPTER - III : EXPERIMENTAL	16
3.1 Materials	16
3.2 Apparatus	19
3.3 Analytical Methods	19
3.4 Experimental Procedure	21

CHAPTER - IV	:	RESULTS AND DISCUSSIONS	24
		4.1 Factor Controlling Efficiency of Phosphate Removal	24
		4.1.1 Effect of PH	25
		4.1.2 Effect of P_i	31
		4.1.3 Effect of R	34
		4.2 Comparison Between Pure and Natural System	34
		4.2.1 Effects of Suspended Solid	37
		4.2.2 Effects of Bio-degradable Organic Matter	39
		4.3 Mechanism of Phosphate Removal from Aqueous Solution by Alum Coagulation	42
		4.3.1 Comparison Between Total Precipitation and Adsorption	44
		4.4 Recommendation	48
		4.5 Suggestions for Future Work	49
CHAPTER - V	:	CONCLUSION	51
BIBLIOGRAPHY			53
APPENDIX - A			
APPENDIX - B			

NOTATIONS

- P_i - Initial Ortho-phorous concentration in the sample as mg/l of Orthophosphate (PO_4).
- P_f - Residual Phosphorous Concentration in the effluent after the alum coagulation treatment as mg/l of Orthophosphate (PO_4).
- R - $Al^{+3} : PO_4^{-3}$ Molar Ratio
- R' - Alum : PO_4^{-3} Weight Ratio
- e - Percentage Removal of Phosphate

LIST OF TABLES

<u>TABLE</u>		<u>Page</u>
1.	Different sources of phosphorous and their concentration.	6
2.	Comparison among several phosphorous removal process.	10
3.	Characteristics of natural waste water used. (IIT/K Campus raw sewage & oxidation pond effluent)	18
4.	Results of the Seperate adsorption process.	46

LIST OF FIGURES

<u>FIGURES</u>	<u>Page</u>
1. Total dissolved phosphorous due to solubility of $Al PO_4$ as a function of PH.	26
2. Total dissolved aluminium due to solubility of $Al PO_4$ and $Al (OH)_3$ as a function of PH	27
3. Effect of PH & R on P_f - Pure System - $P_i = 10 \text{ mg/l}$	28
4. Effect of PH & R on P_f - Pure System - $P_i = 30 \text{ mg/l}$	29
5. Effect of PH & R on P_f - Actual Waste Water (IIT/K Campus raw sewage) - $P_i = 10 \text{ mg/l}$	30
6. Precipitation of orthophosphate by alum coagulation at optimum PH-6-Pure System Graph : P_f VS. R	32
7. Precipitation of orthophosphate by alum coagulation at optimum PH-6-Pure System Graph : e VS R and P_f VS P_i	33
8. Comparison of Phosphate removal between Pure and actual waste water system at optimum PH-6	35

9.	Effect of Suspended solid on phosphorous removal at PH-6	38
10.	Effects of Biodegradable organic matter on phos removal at PH-6.	40
11.	Comparison of phosphate removal from pure solution, Actual sewage and synthetic waste samples.	41
12.	Comparison between total precipitation and adsorption	47
13.	Standard curve (Absorbance VS. Orthophosphate concentration) for orthophosphate determination.	50

ABSTRACT

The removal of ortho-phosphates by alum coagulation has been studied in pure solutions and natural and synthetic waste water samples to investigate the mechanism and effective alum dose requirements. As a detail parametric study, the effects of PH; initial phosphorous concentration (P_i), Alum dose i.e. Al : P molar ratio (R) or Alum : P_i weight ratio (R'); suspended solids and biodegradable organic matter are evaluated in this study. The optimum PH is found to be around 6. At this optimum PH-6 the dose required is $R = 2.0$ or $R' = 7.0$ to achieve effective removal (P_f around 0.5 mg/l) irrespective of P_i in pure system. But this dose requirement becomes higher in case of actual waste water sample and it is found that biodegradable organic matter has got more interference than suspended solid in increasing this dose requirement. Actual increase in dose requirement will depend on the concentration of interfering agents. It is found in case of synthetic sample ($P_i = 10$ mg/l, S.S = 20 mg/l and B.O.D = 20 mg/l) the dose increases by 25% from pure sample and when the concentration of interfering agents is increased more the percentage increase in dose requirement becomes more.

From a separate adsorption study it is seen that the removal of phosphate does not take place only due to the adsorption of phosphate on $\text{Al}(\text{OH})_3$ flocs but a chemical precipitation and adsorption take place simultaneously.

through filter media in the water treatments due to floating algae and aquatic plants, fluctuation of dissolved oxygen concentration in the water body, obnoxious odour and taste are the usual problems created due to eutrophication. So the control of eutrophication is essential.

Now both nitrogen and phosphorous are essential for the growth of algae. So theoretically the growth of algae can be arrested by eliminating either of the nutrients. But although very recent studies (35) have shown the growth rate of algae is much more sensitive in case of nitrogen limiting condition rather than phosphorous limiting condition, the removal of phosphorous has received initial emphasis for two reasons :

- (1) Phosphorous is easier to remove since it forms insoluble compounds and the chemistry seems straight forward.
- (2) Some blue green algae have the capacity of fixing nitrogen from the atmosphere so that phosphorous becomes the limiting nutrient in their life cycle (44).

Regarding removal, about 90% removal of phosphorous is essential to control eutrophication. Such a high

degree of removal can not be achieved in conventional biological treatment. Activated sludge and Trickling Filter can remove 10-30% and oxidation pond can remove up to 60% only. Of-course the modified activated sludge process by extended aeration can remove phosphorous to the desired level but it will involve more cost and at the same time may not be so reliable because in any biological treatment this unreliability is always there. Therefore chemical treatment has received more attention for the removal of phosphorous because both feasibility of high degree of removal and reliability are there.

The chemistry behind the removal of phosphorous by chemical treatment is that bivalent or trivalent metal ion like Ca^{+2} or Fe^{+3} and Al^{+3} can precipitate out the phosphorous by forming the insoluble phosphates. These metal ions can be provided by adding the chemicals : Lime, Ferric Chloride, Alum etc. But which of these Chemicals will be more economic and effective require more detail comparison among them. Lime and Ferric Chloride are cheaper than alum, but these chemicals may cause hardness and colour in turn if not properly controlled. Therefore, in the present study undertaken to determine the mechanism and effective coagulant dose for removal of phosphate from pure solutions and actual waste water system, **alum has been used as the coagulant.**

CHAPTER - 2

LITERATURE REVIEW & OBJECTIVE OF WORK

2.1 FORMS AND CONCENTRATION OF PHOSPHOROUS IN WASTE WATER :

Phosphorous is usually present in waste water in the form of organic phosphorous, inorganic condensed phosphates, and orthophosphates. Most of the organically-bound phosphorous compounds in waste water are present as particulate organic matter and as bacterial cells. Very little is known about the dissolved organic phosphorous compounds which are the by-products of bacterial metabolism and cell lysis. Inorganic condensed phosphates such as pyrophosphate ($P_2O_5^{-4}$) tripolyphosphate ($P_3O_{10}^{-5}$); and trimetaphosphate ($P_3O_9^{-3}$) originate mainly in household detergents. Orthophosphate (PO_4^{-3}) is an end product of microbial degradation of phosphorous-containing organic compounds; orthophosphate is also excreted^{cr} in urine, and is the product of enzymatic hydrolysis of condensed phosphates. Phosphorous in the orthophosphate form is most readily available for biological utilization. The concentrations of the various forms of phosphorous in domestic waste water are subject

to wide hourly and daily fluctuations. Waste waters received at or discharged from different plants also contain varying concentration of phosphates depending on the type of community served and the nature of the biological treatment process employed. According to Ronald, G, Schuessler (31) it is seen that approximately one-third of the total phosphorous is in the soluble orthoform, one-third in the soluble poly form, and one-third in the suspended form. Weinstein and Hunter as quoted by Ghassemi (15) studied phosphate concentration in three Activated Sludge and three trickling filter plants and found that in the influent to the biological treatment units inorganic condensed phosphates constituted 15 to 75% of the total phosphorous and that about 50% of the condensed phosphates were hydrolyzed to ortho-phosphate on their passage through the treatment plants. C.N. Sawyer (36) reported that hydrolysis of inorganic complex is hindered at low temperature and that TPP (Sodium tripolyphosphate: $\text{Na}_5 \text{P}_3 \text{O}_{10}$) is hydrolyzed much more slowly than TSPP (tetra sodium pyrophosphate: $\text{Na}_4 \text{P}_2 \text{O}_5$). Rolf Eliassen and George Tchobanoglous (13) reported the various sources and the concentration of total phosphorous present in each source as follows :

TABLE-1

<u>Sl. No.</u>	<u>Sources</u>	<u>Total Phosphorous (mg/l as P)</u>
1.	Domestic Waste	3.5 - 9
2.	Rural Runoff :	
	(a) Agricultural land	0.05 - 1.1
	(b) Nonagricultural land	0.04 - 0.2
3.	Urban Runoff	0.1 - 1.5
4.	Rain fall	0.01 - 0.03
5.	Industrial Waste	

The above data were reported in 1968 and some 15 years earlier Sawyer (36) had reported the total phosphorous concentration in domestic waste water to be 2-4 mg/l as P. Such a difference in concentration within one decade was due to the increase of synthetic detergents' use for household purpose at the rapid rate. Total phosphorous concentration of I.I.T/Kanpur Campus sewage was found to be 5.5-6 mg/l as P (39) and out of which, orthophosphate Conc was 3.0 - 3.3 mg/l as P (author, 1971).

2.2 LEVEL TO WHICH THE PHOSPHOROUS SHOULD BE REMOVED

After knowing the forms and conc of phosphorous in which it is present in waste water, the next important criterion is the level of removal. At present, one of the major difficulties in designing or planning for the removal of phosphorous is that reliable information is not available regarding the levels to which it must be removed to minimize or eliminate the adverse effect caused by its discharge. Up till now there appears to be no general agreement as to the level to which phosphorous must be reduced before the effluent can be discharged. Sawyer (36) suggested a limiting value of .01 mg/l of inorganic phosphorous based upon his observation of 17 Wisconsin Lakes. On the other hand Dryden as quoted by Ghassemi (15) originally proposed a limit of 2 mg/l as PO_4 (0.65 mg/l as P) for a recreational lake supply but later revised this down to 0.5 mg/l as PO_4 (.16 mg/l as P) as necessary to prevent regrowth of algae. This sort of disagreement can be solved by studying the growth of mixed culture of algae in different cases : (i) N-enriched media; (ii) P-enriched media (iii) Neutritionally balanced media. According to J.H. Ryther and W.M. Dunstan (35) the uptake of N and P takes place in the ratio of N to P from less

than 3:1 to over 30:1 (by atoms). The ratio varies depending on the kind of algae grown and the availability of nutrient and the average optimum N to P ratio can be accepted as 10:1 because values between 5:1 and 15:1 are most commonly encountered. Such a study will not only set a permissible value of phosphorous or Nitrogen Concentration in a pond or stream to stop the nuisance growth of algae but also will dictate whether the productivity of algal mass is sensitive in case of Nitrogen limiting or phosphorous limiting condition.

2.3 REMOVAL METHODS :

The most common methods of waste water treatment involve biological oxidation. The microorganisms present in the waste water degrade the complex organic molecules into simpler products thereby acquiring energy and materials for their growth and the synthesis of new cells. As the supply of the available food diminishes, the starving bacteria agglomerate into large flocs which are removed by settling. Although conventional biological treatment processes can result in a substantial reduction of the carbonaceous organic matter, only 10-30% of the phosphorous compounds initially present in the raw waste water is converted into removable cell material due to the unique

nutritional requirements of sewage bacteria. Conventional Activated Sludge and Trickling filter process can remove 10-30% whereas the oxidation pond can remove a little more (about 60%). Therefore, the effluents from most conventional biological treatment units still contain substantial quantities of phosphates which have to be essentially completely removed if serious deterioration of water quality in the receiving streams is to be avoided. Ofcourse several investigators (9,18,25,32,33) have shown that significant removal about 80-90% can be achieved by modifying the conventional Activated Sludge parameters : Dissolved oxygen, biochemical oxygen demand to activated sludge loading, mixed liquor suspended solids and return sludge rate. Previous work shows that in order to attain maximum phosphorous removal, dissolved oxygen should not drop below 2 mg/l in more than one-half of the aeration tank and should react the level of about 5 mg/l at the end, but avoid over aeration; B.O.D to activated sludge loading should be 50 lbs. B.O.D. per 100 lbs. of aeration solids and sludge settle index should be about 150. The modifications of the parameters will involve more cost and at the same time it may not be so reliable because in biological process it is always there. So the Biological Process is not so suitable for phosphorous removal.

TABLE - 2

COMPARISON AMONG SEVERAL HOSINGONS REMOVAL PROCESS(13)

Sl. No.	Process	Removal effy. (%)	Cost (\$/MG)	Type of waste to be disposed
1.	Biological Treatment	10-30	30-100	Sludge
2.	Modified Activated Sludge Process	60-80	30-100	"
3.	Chemical Precipitation	83-95	10-70	"
4.	Sorption	90-98	40-70	Liquid & Solid
5.	Ion Exchange	86-98	170-300	Liquid
6.	Electrochemical Treatment	81-85	-	Liquid and Sludge
7.	Electrodialysis	30-50	100-280	Liquid
8.	Reverse Osmosis	65-95	250-400	"
9.	Distillation	90-98	400-1000	"
10.	Land Application	60-90	95-150	None

Among chemical methods, Ion exchange process is impractical to implement because it requires extensive pretreatment for reducing the organic matter fouls the resin. However the recent development of macroporous resin which will absorb much organic matter without fouling and the possibility of less expensive regeneration chemicals, makes this process worth consideration again.

Of all other chemical methods available for the removal of phosphates, chemical precipitation using Aluminium Ferric and Calcium Salts has received the widest attention. Aluminium Salts (Alum) has been preferred although it is costlier than Ferric and Calcium Salts perhaps because of two reasons:

(1) The optimum PH for maximum phosphorous removal in case of Ferric and Calcium Salts are around 5.0 and 11.0 respectively both of which do not correspond to the PH of Natural waste water and so the adjustment of this optimum PH will involve more cost.

(2) If the doses (Fe , Ca) are not properly controlled, this may cause colour and hardness respectively in turn.

Lea et al (21) reported from their laboratory pilot plant study that to achieve a residual phosphorous concentration in the effluent (P_f) of 0.5 mg/l as PO_4 from an initial Phos. Conc. (P_i) of 13.8 mg/l as PO_4 an alum dose of 200 mg/l was required at optimum ^{PH} ~~by~~ range 7.1-7.7. Stumm (42) found this optimum PH to be 6.3. Again Eberhardt (12) showed that to achieve $P_f = 0.5$ mg/l as PO_4 from $P_i = 40$ mg/l as PO_4 Alum. dose required was 210-294 mg/l whereas Timney, concluded the dose required was higher around Al^{+3} to P_i molar ratio 3.5:1.

2.4 MECHANISM OF REMOVAL :

A knowledge of the Mechanism of phosphate removal is important to investigate the discrepancies among the investigators as discussed above. Once the mechanism is known we can investigate the possible interfering parameters making the results inconsistent from investigator to investigator. Unfortunately the actual mechanism has not yet been well defined in case of phosphorous removal by Alum Coagulation. A number of investigators (42 etc.) believe that phosphate is removed from aqueous solution in the form of the precipitate, $AlPO_4$ whereas other investigators (21) believe that the adsorption of phosphate on the $Al(OH)_3$ flocs is mainly responsible for removing

phosphate from aqueous solution by alum coagulation. Those who support the adsorption mechanism have shown that the results of phosphorous removal by alum coagulation can be plotted satisfactorily in Freundlich adsorption isotherm. But the satisfactory plot of the results in Freundlich adsorption isotherm is no indication that adsorption is the only mechanism taking place because the result of simple precipitation can also be plotted in Freundlich adsorption isotherm. On the other hand, those who support the precipitation of AlPO_4 can not say conclusively that the precipitate being formed is only AlPO_4 .

If a stoichiometric compound AlPO_4 is precipitated, maximum removal should be achieved when Al^{+3} to PO_4^{-3} molar ratio in solution is 1:1. However, none of the investigators found this to be true. It is almost certain that along with AlPO_4 some hydroxide of Al is also precipitated which may or may not adsorb phosphate ions. Popel (30) has derived a mathematical model applying the Freundlich adsorption equation to precipitation of a mixed Al hydroxy-phosphate in which PO_4 ions compete with OH ions.

2.5 OBJECTIVE :

In any removal process whether it is physical, chemical or biological, the most fundamental and important part of the process is to know the mechanism of removal. But from the literature review of the removal of phosphorous by Alum Coagulation it appears that the mechanism is not yet well defined. There is an uncertainty whether phosphorous is removed due to straight and simple chemical precipitation of $AlPO_4$ or due to the adsorption of phosphate on the flocs of $Al(OH)_3$. So my first objective is to clarify these uncertainties regarding the phosphorous removal by Alum Coagulation. Apart from the mechanism of removal there are some other criteria which are to be developed for the use by Engineers in the design and operation of the process. Those criteria are : the effects of PH; initial phosphorous concn (P_i) coagulant dose; reaction time, flocculation time, settling time and characterization of sludge. Among these criteria the most important one is the coagulant dose. Much of the economy depends on the effective and accurate determination of the coagulant dose. But from the literature review it is found that the dose requirements for effective removal of phosphorous varies from investigator to investigator.

This essentially may be due to P_1 , FH and waste water characteristic (suspended solids, Biochemical oxygen demand, other dissolved ions.) So by another objective is to study the effects of the above mentioned parameters on the coagulant dose for effective removal and to see what actually made the previous investigators' result inconsistent and also thereby to predict the actual dose requirement considering the effect of those parameters.

So in short the objectives of this work can be stated as follows:

- (1) To investigate the actual mechanism takes place in the removal of Phosphate by Alum coagulation.
- (2) To find out the actual coagulant dose requirement for effective removal.

CHAPTER - III

EXPERIMENTAL

3.1 MATERIALS :

The following chemicals and others have been used in preparation of various reagents and to carry on the experiments:

- (1) Potassium di-hydrogen Phosphate (KH_2PO_4)
- (2) Stannous Chloride ($\text{SnCl}_2, 2\text{H}_2\text{O}$)
- (3) Ammonium Molybdate $\left[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}, 4\text{H}_2\text{O} \right]$
- (4) Aluminium Sulfate $\left[\text{Al}_2(\text{SO}_4)_3, 18\text{H}_2\text{O} \right]$: Alum
- (5) Peptone
- (6) Kaoline Powder
- (7) Glycerine
- (8) Sulfuric Acid (H_2SO_4)
- (9) Sodium Hydroxide (NaOH)
- (10) Distilled Water
- (11) I.I.T/K - Campus Raw Sewage
- (12) I.I.T/K - Campus Oxidation Pond Effluent

Potassium di-hydrogen phosphate has been used to prepare pure ortho-phosphate solution. A stock solution

(500 mg/l as PO_4) was prepared and whenever the pure orthophosphate solutions of various concentration (4.0, 10.0, 20.0, 30.0 mg/l as PO_4) have been required, they have been prepared by diluting the stock solution with distilled water.

Stannous chloride, Ammonium Molybdate, Glycerine, conc. sulfuric acid have been used to prepare stannous chloride solution and acid ammonium molybdate results required for the analysis of orthophosphate in solution. These reagents have been prepared as per standard methods.

Peptone and Kaoline Powder have been used as representative of B.O.D and S.S. in synthetic sample respectively. C.O.D. contribution of peptone is assumed to be 0.2 gm/gm. On the basis of this data 1250 mg/l and 125 mg/l of peptone has been used to represent B.O.D. of 200 mg/l and 20 mg/l respectively. B.O.D has been taken as 80% of C.O.D.

N/10 Sulfuric Acid and N/10 Sodium Hydroxide have been used for pH adjustments.

All the chemicals used were the purest grade available.

The characteristics of the phosphorous containing natural waste water (I.I.T/K Campus raw sewage and oxidation

pond affluent) used in the experiments are given below:

TABLE - 3

CHARACTERISTICS OF WASTE WATER USED

<u>Sl.No</u>	<u>Parameter</u>	<u>ML/K campus raw sewage</u>	<u>Oxidation Pond Effluent</u>
1.	Temp. °C	25-26	29-31
2.	Total solids mg/l	1023	860
3.	Total suspended solids mg/l	467	-
4.	Volatile suspended solid mg/l	210	-
5.	Volatile dissolved solids mg/l	240	-
6.	Amonia Nitrogen mg/l	6.5	2.83
7.	Organic Nitrogen mg/l	8.0	5.2
8.	Total Phosphorous mg/l as P	5.2	2.8
9.	Total orthophosphate mg/l as PO_4	10.0	4.0
10.	PH	7.9	8.8
11.	COD mg/l	279	-
12.	BOD, 5 day ,20°C, mg/l	136	25
13.	BOD Ultimate mg/l	210	135
14.	Flow 10^6 l/d	2.8	2.7
15.	Algae conc. mg/l	-	412
16.	D.O mg/l	-	8.9

3.2 APPARATUS :

The following apparatus are used to carry on the experiments .

1. Phipps and Bird Six place stirrers (Phipps and Bird, Inc. Richmond, Va)
2. Beckman Expandometric pH meter (Beckman Instrument Co., Fullerton, Calif.)
3. EILCO PH meter model LM -10 (Electronic & Industrial Instrument Co.Pvt. Ltd. Hyderabad, India)
4. Bausch and Lomb Spectronic 20 Calorimeter/
Spectrophotometer (Bausch and Lomb Co. Rochester, N.Y.)
5. 25 KV X-ray Diffractometer.

All "Jar Test" precipitation experiments were conducted using apparatus 1. The Apparatus 2 & 3 were used for pH measurement. Most of the time apparatus 2 was used. Calorimetric analyses were made with apparatus 4. and X-ray diffraction analysis was made on apparatus 5.

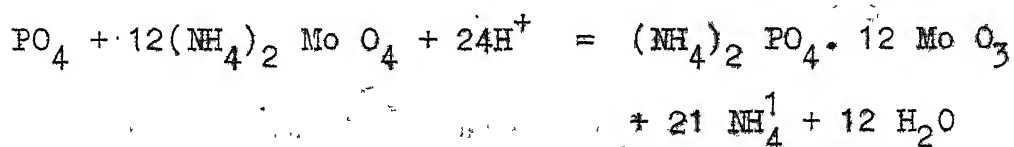
3.3 ANALYTICAL METHODS :

All through these experiments only orthophosphates in solution have been considered. The Quantitative determination of orthophosphates can be done by Gravimetric,

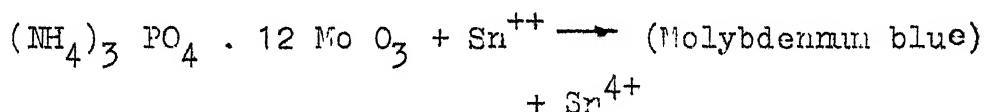
volumetric and colorimetric methods. The gravimetric method is applicable where, large amounts of phosphorous are present, but such situations do not occur in sanitary engineering practice. The volumetric method is applicable when phosphate concentrations exceed 50 mg/l, but such concentrations are seldom encountered except in boiler waters and digester supernatant liquors. Since the concentration of phosphate usually occur in the waste water are less than 50 mg/l, colorimetric method was chosen for quantitative determination of phosphate.

Of the two colorimetric methods the stannous chloride method described in standard method was used for determination of orthophosphate throughout the experiment. The principle of the method is to develop a colour and to determine the intensity of the colour by colorimeter or spectrophotometer. The chemistry involved is essentially as follows :

Phosphate ion combines with ammonium molybdate under acid condition to form a complex compound known as ammonium phosphomolybdate.



The molybdenum contained in ammonium phosphomolybdate is readily reduced by Sn^{+2} to produce a blue coloured sol. that is proportional to the amount of phosphate present. The coloured compound formed has never been isolated and its formula is unknown. The chemistry involved with stannous chloride as the reducing agent, may be represented in qualitative manner as follows :



The absorbance of this blue colour developed for 10 mts is measured with spectronic-20 at 690 m μ wave length and then from the standard curve phosphate conc Vs Abs . the actual concentration of phosphorous is calculated.

3.4 EXPERIMENTAL PROCEDURE :

All the experiments were carried out in 'Batch Process'. The procedure of the experiment can be described as follows : 500 ml. of the sample is taken in each of the six 1 l beakers. Calculated amounts of alum solutions (freshly prepared) are added to the sample so that the molar ratio $R = \text{Al/P}$ varies in the range - 1.0, 1.5, 2.0, 2.5, 3.0, 5.0. Then the electrodes of the PH meter were

dipped into the sample and PH of the sample is adjusted to 4.0, 5.0, 6.0, 7.0 8.0, 9.0 by adding N/10 H_2SO_4 or N/10 Na OH. After the adjustment of PH the beakers are placed in Phipps and Bird six place stirrer (Jar Test Apparatus) and for first 2 minutes samples were rapidly stirred at 100 r.p.m. and then the stirring is gradually slowed to 20 r.p.m. and kept on stirring at 20 r.p.m. for 20 minutes. After the flocculation the samples were allowed to settle for overnight and then the effluents were analysed to find out the concentration of phosphate.

The following samples containing phosphorous have been considered in the experiments.

1. Pure test solution of orthophosphate in distilled Water of varying concentration $P_i = 4.0, 10.0, 20.0, 30.0$ mg/l as PO_4 .

2. Actual waste water : (i) I.I.T/K Campus Raw Sewage ($P_i = 10.0 \pm 0.5$ mg/l as PO_4) and (ii) I.I.T/K Campus Oxidation Pond effluent ($P_i = 3.5 \pm 0.5$ mg/l as PO_4).

3. Synthetic Sample :

S_1 : $P_i = 10$ mg/l ; S.S = 20 mg/l

S_2 : $P_i = 10$ mg/l ; S.S = 1000 mg/l

S_3	:	$P_i = 10 \text{ mg/l}$;	$B.O.D = 20 \text{ mg/l}$
S_4	:	$P_i = 10 \text{ mg/l}$;	$B.O.D = 200 \text{ mg/l}$
S_5	:	$P_i = 10 \text{ mg/l}$;	$S.S = 20 \text{ mg/l}, B.O.D = 20 \text{ mg/l}$
S_6	:	$P_i = 10 \text{ mg/l}$;	$S.S = 1000 \text{ mg/l}, B.O.D = 200 \text{ mg/l}$

The effects of PH variation 4 to 9 were studied in case of three samples : (i) Pure Phosphate solution (10 mg/l) (ii) Pure Phosphate solution (30 mg/l) and (iii) Actual waste water - I.J.T/K Campus Raw Sewage ($P_i = 10 + 0.5 \text{ mg/l}$).

In cases of all other sample the experiments were conducted at optimum PH - 6.0.

Another experiment to study the adsorption process separately was carried out. Here what was done is as follows : 490 ml. of distilled water is taken in each of the six 1 litre beakers. The electrodes of the PH meter were dipped into the D.W and the PH (7.2) is recorded. Then 1.0, 1.5, 2.0 5.0 ml of Alum solution (17.5 gm/l) are added, the PH falls to 4.55, 4.5 4.2 accordingly which were brought to around 6.5 by adding N/10 Na OH to form $Al(OH)_3$ flocs and after the formation of $Al(OH)_3$ flocs 10 ml. of Phosphate Stock solution (500 mg/l) is added to each of the six beakers. Slight changes (decrease) in PH were observed. Then the sample were flocculated and settled as like before and the concentration of phosphorous was measured.

CHAPTER - IV

RESULTS AND DISCUSSION

4.1 FACTORS CONTROLLING EFFICIENCY OF PHOSPHATE REMOVAL :

The efficiency of Phosphate removal by a given process is defined as :

$$e = \frac{P_i - P_f}{P_i} \times 100$$
$$= \left(1 - \frac{P_f}{P_i} \right) \times 100$$

where, P_i = Initial Phosphorous Concentration in the Influent.

P_f = Final (residual) Phosphorous Concentration in the effluent.

A review of previous work shows that e is dependent on three factors : P_i ; PH of the effluent and R (alum dose expressed as Al:P molar ratio in the treated solution). These three factors have not been studied together in a single investigation so far. On the other hand, it is obvious that the alum dose required for a desired efficiency will depend on PH and P_i . With this end in view PH, P_i and

R were varied separately in controlled experiments and the following results were obtained.

4.1.1 EFFECT OF PH :

If phosphate is removed, at least partly, by precipitation of Al-Phosphate compounds the process should be strongly PH dependent on theoretical grounds. Figures 1. and 2 show the solubility of AlPO_4 and $\text{Al}(\text{OH})_3$ as a function of PH calculated on the basis of available thermo-chemical data. Details of their calculations are supplied in the Appendix. It is clear that AlPO_4 , $\text{Al}(\text{OH})_3$ or a mixture of the two have solubility minima between PH 6 and 6.5. This PH range is therefore, optimum for removal of Phosphate by Al-salts.

Figures 3 to 5 show the results of the present series of experiments in which P_f was measured at various PH values with constant P_i and R. It is seen that P_f is minimum around PH-6 for all values of P_i and R for pure phosphate solutions as well as for the raw sewage sample. In addition the pure samples with $P_i = 30 \text{ mg/l}$ retain a minimum P_f not only at PH-6 but for the extended range PH 5 to 7. These PH values for maximum phosphate agree with the theoretically predicted optimum PH for phosphate precipitation.

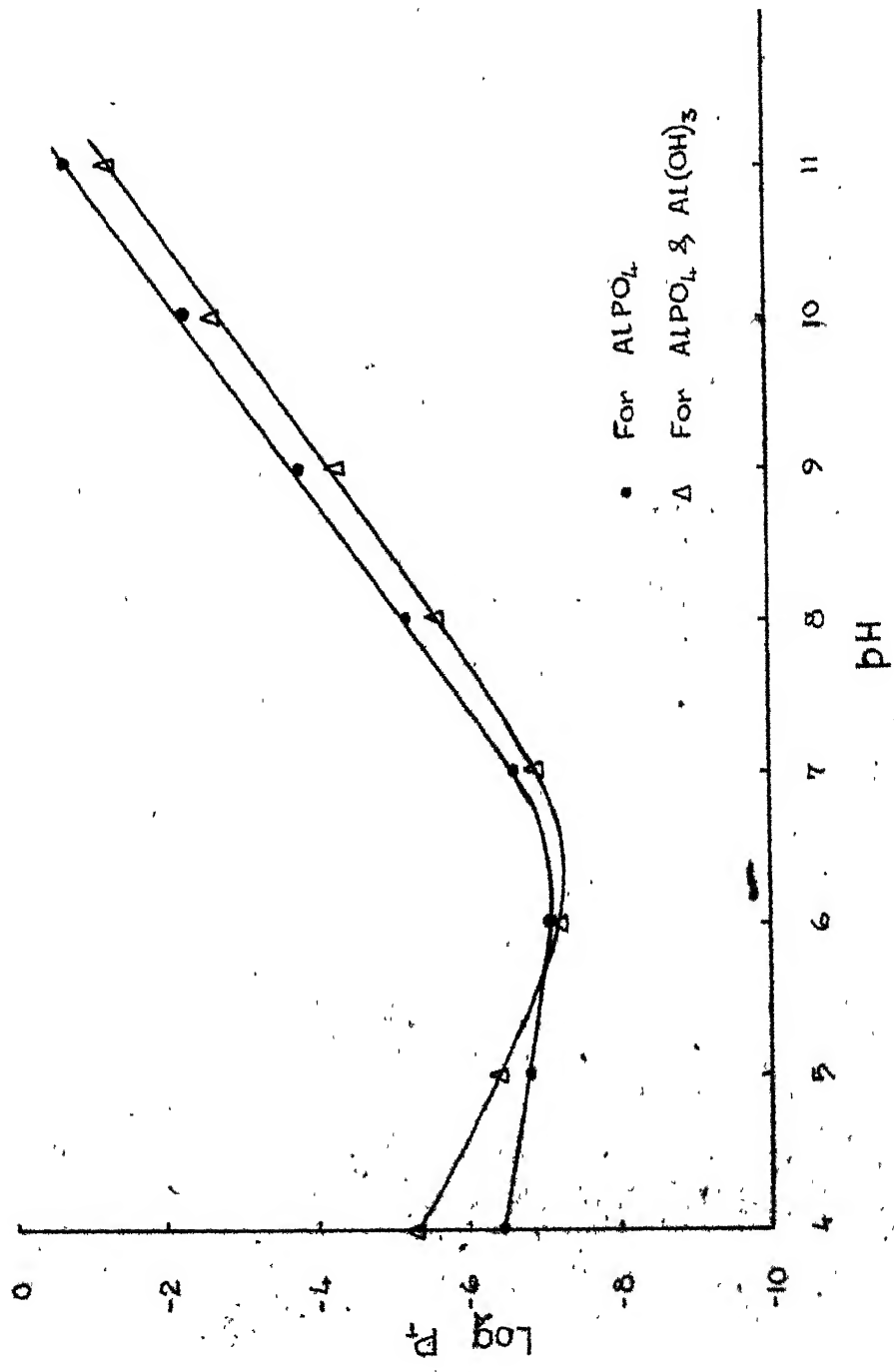


Fig 1. Total Dissolved Phosphorous due to Solubility of AlPO_4 as a function of pH.

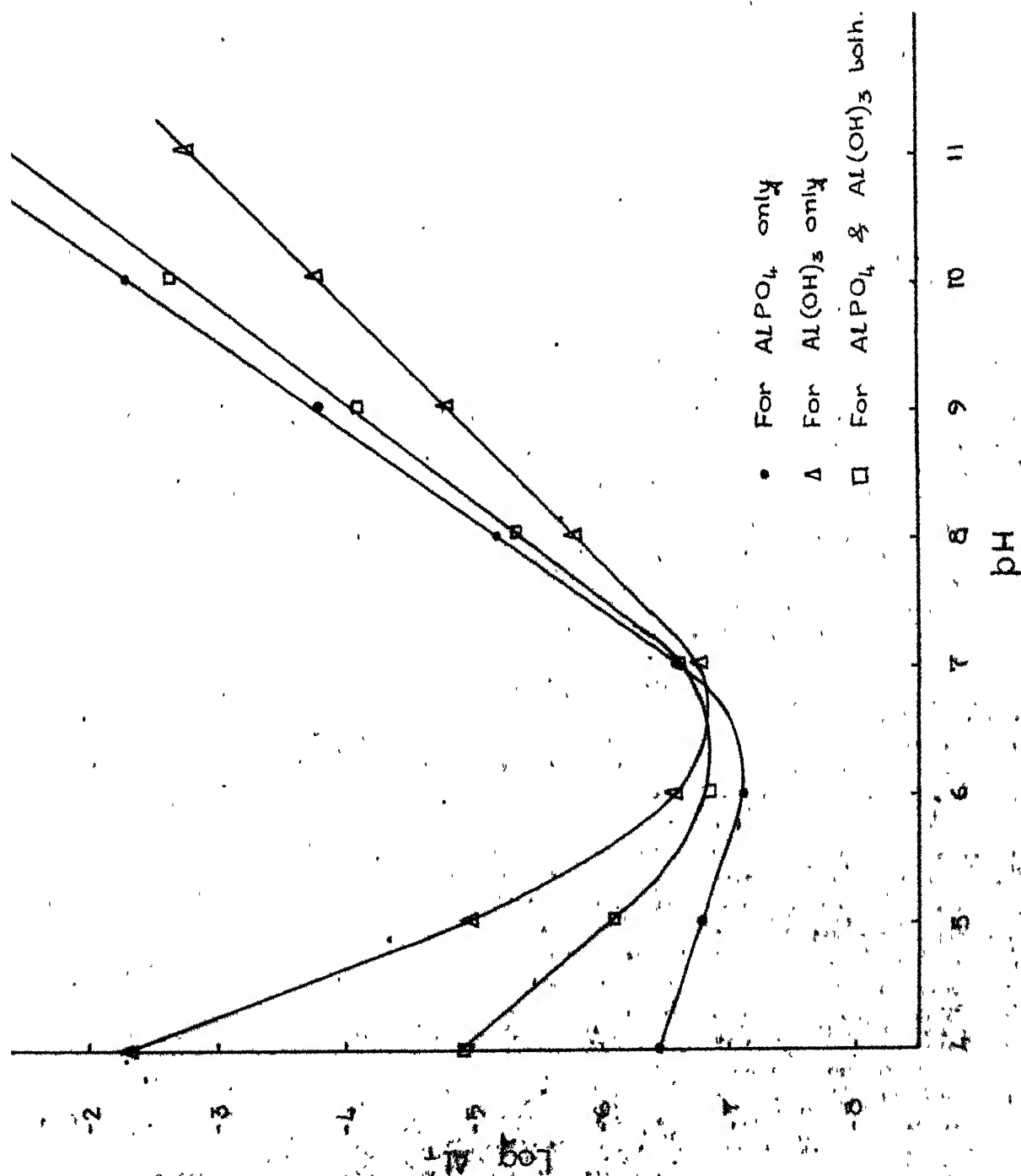


Fig 2: Total Dissolved Aluminium due to Solubility of ALPO_4 & $\text{Al}(\text{OH})_3$ as a function of pH.

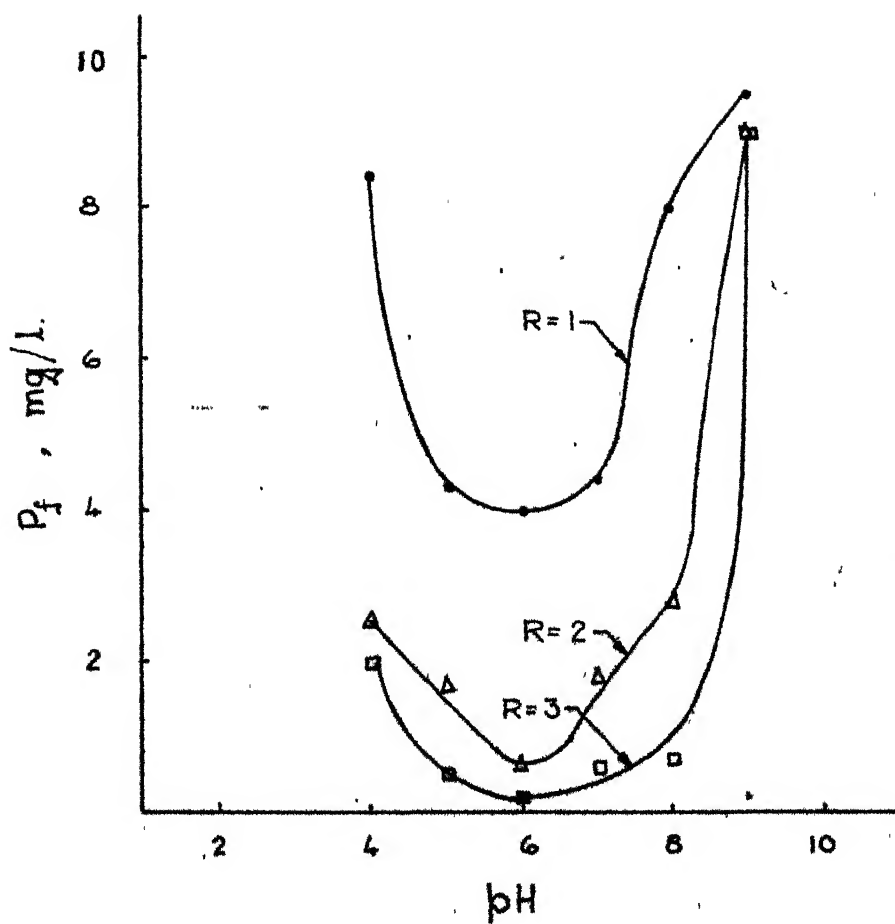


Fig 3. Effect of pH and R on P_f
 Pure System.
 $P_i = 10 \text{ mg/L}$.

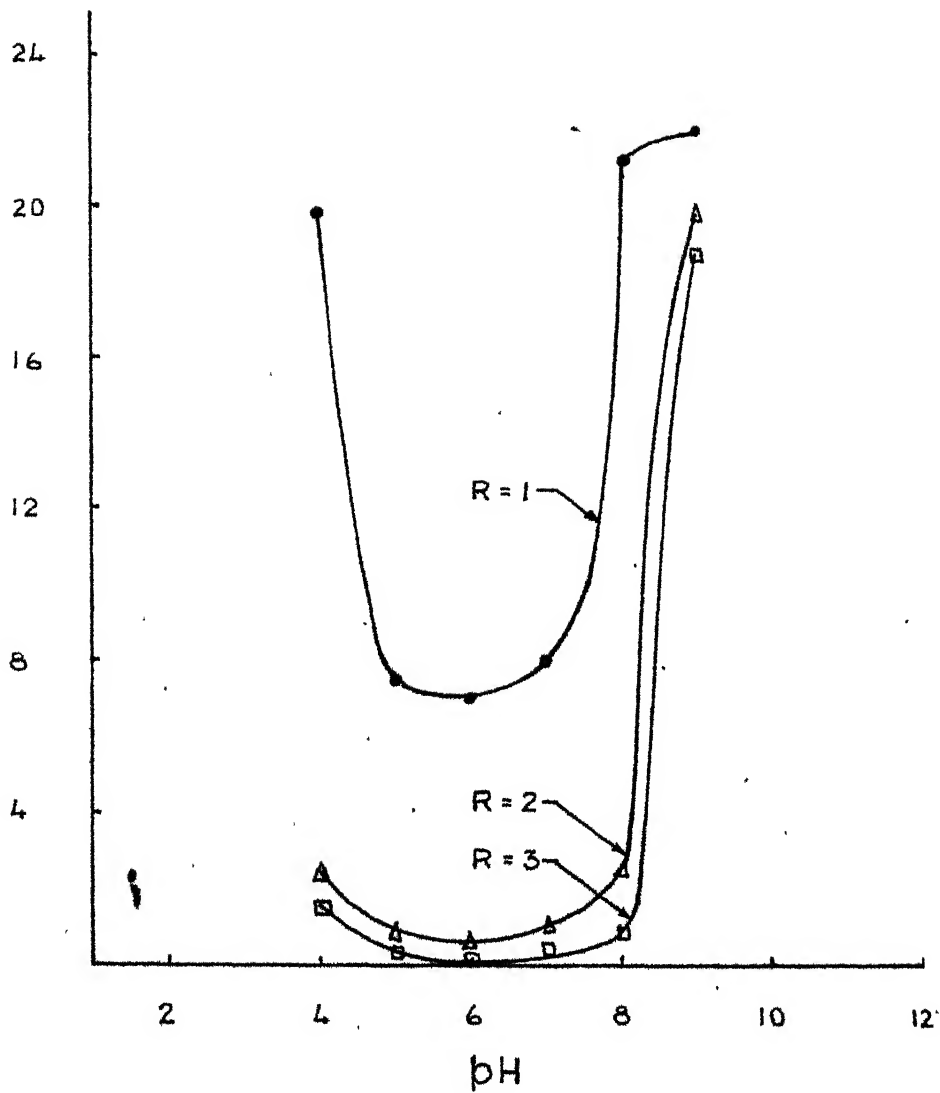
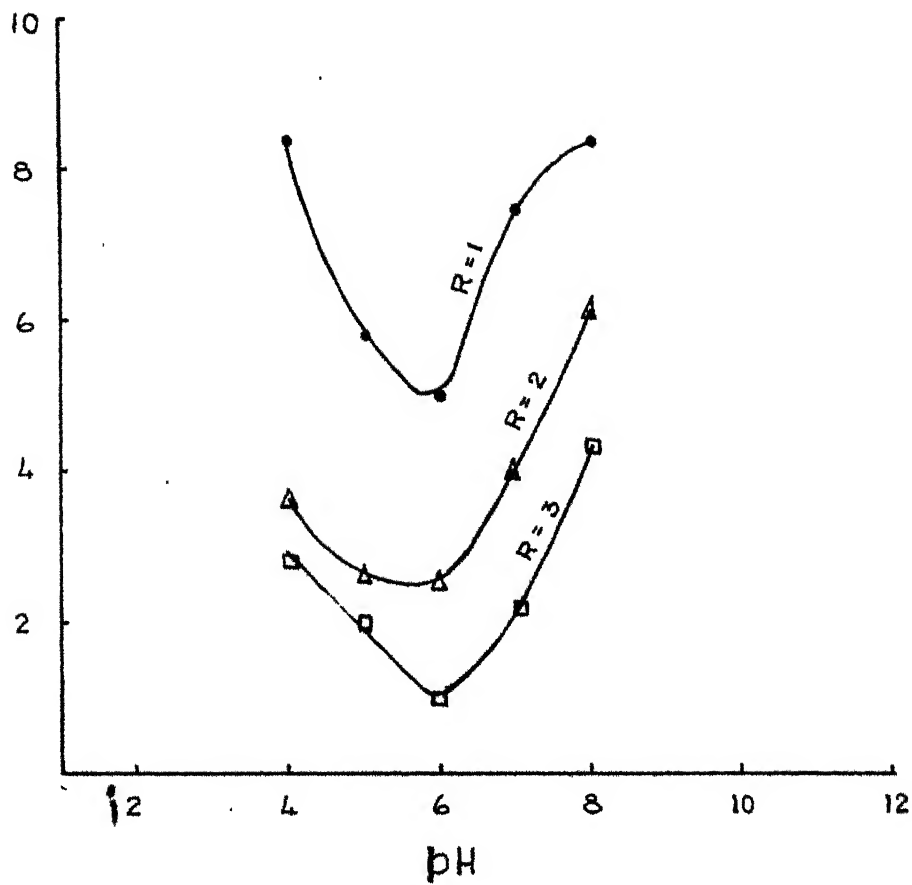


Fig. 4. Effect of pH & R on P_f
 Pure System
 $P_i = 30 \text{ mg/l.}$



Effect of pH & R on P_f

Actual Waste Water

(I.I.T/K Campus Raw Sewage)

$P_i = 10.0 \pm 0.5 \text{ mg/l.}$

4.1.2 EFFICIENCY P_f :

Figure 6 is a plot of P_f against R for solutions of various P_i but PH constant at the optimum value of 6. It is seen that for low alum doses ($R < 2.0$) P_f is higher for higher levels of P_i at a given R . However the rate of increase of P_f is not constant through the entire range of P_i as seen from Fig. 7b. P_f increases linearly at first with P_i and then deviates from a straight line for $P_i > 10 \text{ mg/l}$. The slope of the straight line decreases with increasing R and it becomes parallel to P_i - axis, at $R \geq 2.0$. At $R=2$ P_f values for all P_i converge to 0.6 mg/l (Fig. 6 and 7b).

Because of this manner of increase of P_f with P_i at $R < 2.0$, the ratio P_f/P_i decreases with increasing P_i . Therefore, $e = 1 - P_f/P_i$ increases with increasing P_i as shown in fig. 7a. In other words for a given alum dose in this range, the efficiency of phosphate removal increases with solutions of higher initial concentration of dissolved phosphate.

Conditions are different when the alum dose is high ($R \geq 2.0$). Here P_f is more or less independent of P_i at a given R (Fig. 6). The ratio P_f/P_i decreases and the efficiency of removal (e) increases with increasing P_i (Fig. 7a) and attains a constant value at high R as explained below.

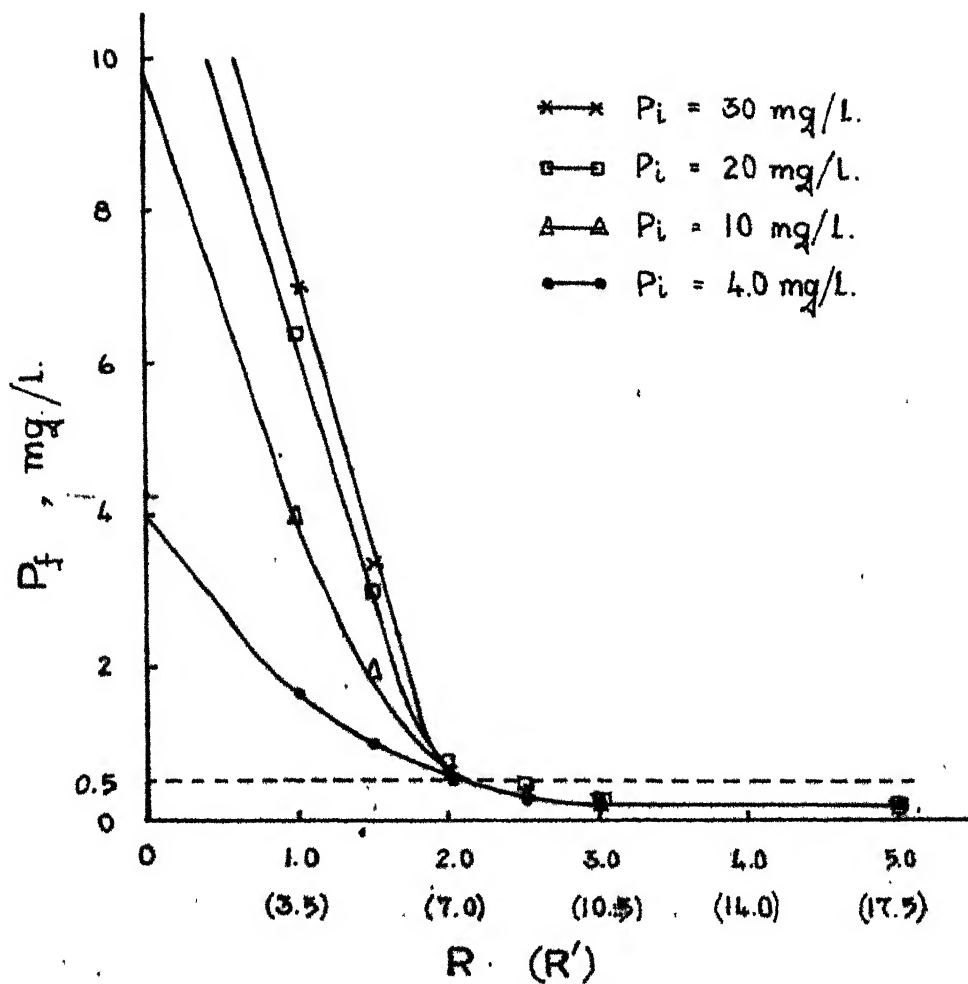


Fig 6. Precipitation of Orthophosphate
By Alum Coagulation
at optimum pH = 6
Pure System

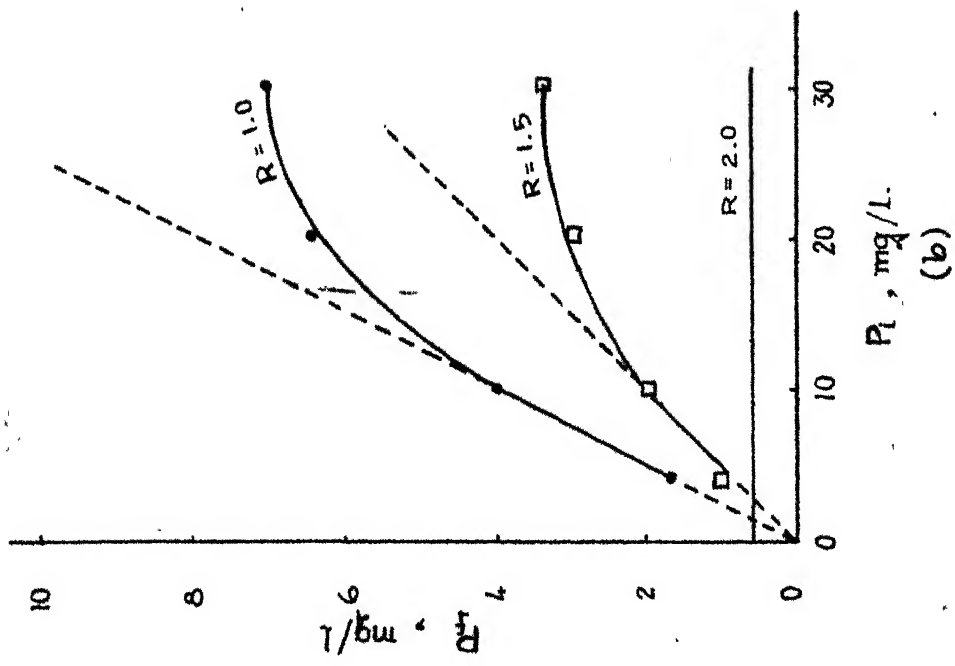
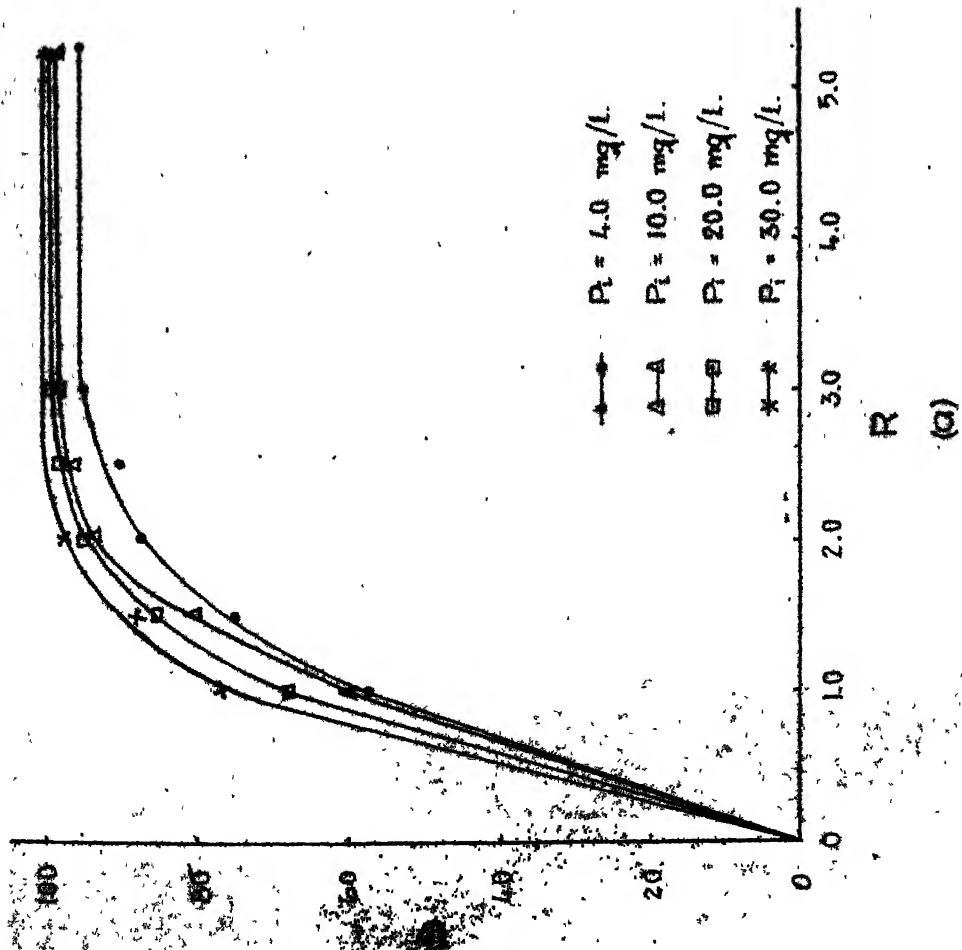


Fig 7. Precipitation of Orthophosphate by Alum Coagulation at Optimum pH-6 in Pure System

4.1.3 Efficiency

All through the above discussion it is implicit that the alum dose (R) plays an important role in controlling efficiency (e) of phosphate removal. The fact that differences in P_F with P_i are eliminated when $R > 2.0$ suggests that $R = 2.0$ is the minimum alum dose necessary for effective phosphate removal. However, P_i changes negligibly between $R = 1.0$ and $R = 2.0$ and becomes practically constant after further increase of R . This shows that the maximal efficiency is reached very soon after $R = 2.0$ (fig. 7a) and the ratio P_F/P_i is constant for a given P_i at higher values of R . In other words, alum dose higher than $R = 2.0$ would not lower P_F at any P_i and the efficiency cannot be improved by any significant amounts.

4.2 COMPARISON OF PURE LABORATORY SYSTEM AND NATURAL SYSTEM :

In pure system alum coagulation was conducted in pure orthophosphate solution prepared from laboratory reagents and natural system alum coagulation was conducted in actual waste water samples. As an actual waste water samples IIT/K Campus raw sewage ($P_i = 10.0 \pm 0.5$ mg/l) and oxidation pond effluent (O.P.E) ($P_i = 3.5 \pm 0.5$ mg/l). The detail comparison is shown in fig. 8. It shows that to achieve same degree of removal the dose requirement

4.1.3 Efficiency

All through the above discussion it is implicit that the alum dose (R) plays an important role in controlling efficiency (e) of phosphate removal. The fact that difference in P_f with P_i are eliminated when $R > 2.0$ suggests that $R = 2.0$ is the minimum alum dose necessary for effective phosphate removal. However, P_f changes negligibly between $R = 2.0$ and $R = 7.0$ and becomes practically constant after further increase of R . This shows that the maximum efficiency is reached very soon after $R = 2.0$ (fig. 7a) and the ratio P_f/P_i is constant for a given P_i at higher values of R . In other words, alum dose higher than $R = 2.0$ would not lower P_f at any P_i and the efficiency can not be improved by any significant amounts.

4.2 COMPARISON BETWEEN PURE SYSTEM AND NATURAL SYSTEM :

In pure system alum coagulation was conducted in pure orthophosphate solution prepared from laboratory reagents and natural system alum coagulation was conducted in actual waste water samples. As an actual waste water samples IIT/K Campus raw sewage ($P_i = 10.0 \pm 0.5$ mg/l) and oxidation pond effluent (O.P.E) ($P_i = 3.5 \pm 0.5$ mg/l). The detail comparison is shown in fig. 8. It shows that to achieve same degree of removal the dose requirement

Pt, mg/L

10

8

6

4

2

0

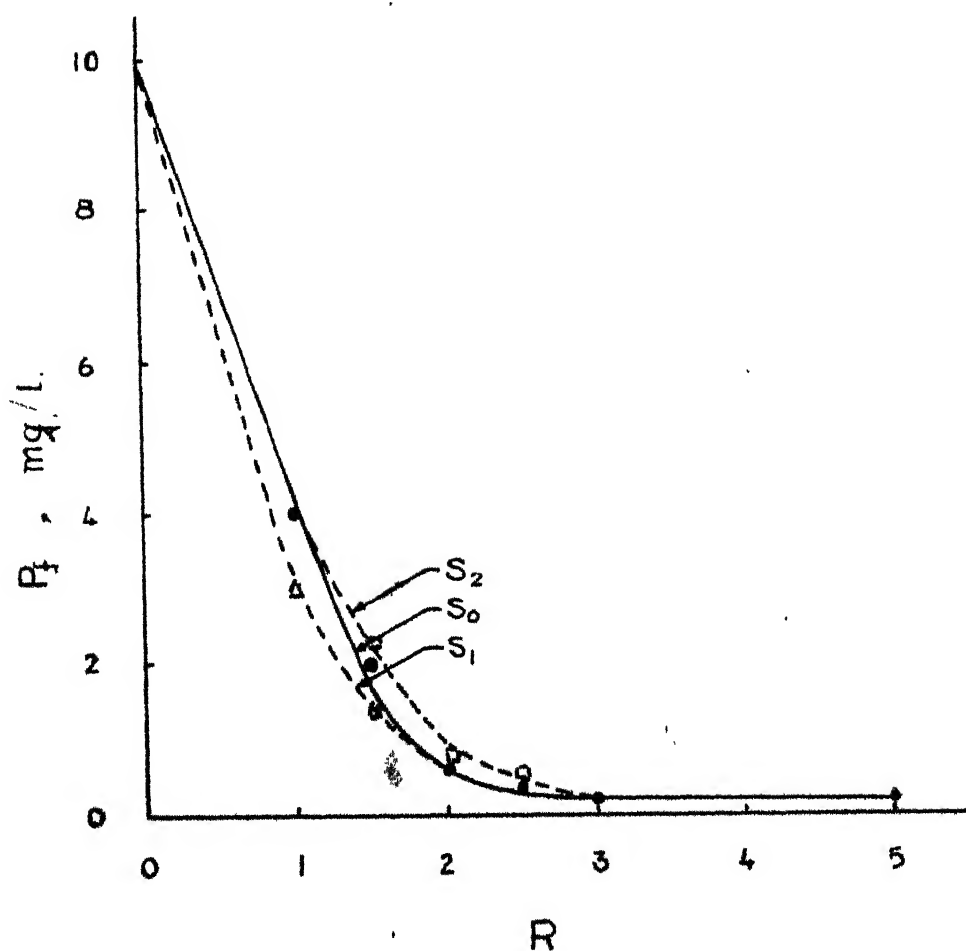


remains same as in pure system for oxidation pond effluent but the dose requirement varies from that of pure system for raw sewage. For raw sewage to achieve $P_f = 0.5 \text{ mg/l}$ at optimum PH-6 the dose necessary is $R = 3.5$ instead of $R = 2.0$ for pure system. This deviation may be due to waste water characteristics because the other parameters affecting efficiency P_i and PH were kept same for both cases (Pure and Natural) in order to compare the results. Oxidation pond effluent can be characterised as having very low B.O.D., significant suspended solid in the form of algal biomass and total dissolved phosphorous is more or less equal to total orthophosphate where as raw sewage can be characterised as having high B.O.D, high suspended solids in particulate and colloidal form and along with ortho-phosphate there is condensed phosphate to a little extent. So it can be concluded that very low B.O.D. and algae do not interfere in the removal of orthophosphate by alum coagulation but very high B.O.D and suspended solids in particulate or colloidal form may interfere in the removal of orthophosphate. The increase in dose for case of raw sewage may be due to extra amount of condensed phosphate which was not taken into account or due to high B.O.D & S.S. To check on this possibility:

Whether B.O.D & S.S. do interfere in the removal of orthophosphate, a few experiments were carried out with suspended solids and biodegradable organic matter added to the pure system. The results are discussed below.

4.2.1 EFFECT OF SUSPENDED SOLIDS :

Effect of suspended solids was studied by conducting coagulation experiment at PH-6 in synthetic sample prepared by adding kaoline powder in various concentration (20 mg/l & 1000 mg/l) to the pure phosphate solution ($P_i = 10 \text{ mg/l}$). Detail comparison of the results between pure and synthetic sample is shown in fig. 9. It appears from the graph that the effect of suspended solid on alum dose requirement for phosphate removal is not very important. Particularly the lower concentration (20 mg/l) which is usually present in the effluent from biological treatment processes (A.S. or T.F.) does not affect at all. The dose requirement remains the same as required in the case of pure phosphate solution. Very high concentration (around 1000 mg/l) of suspended solid may affect a little bit but it is not so much significant.



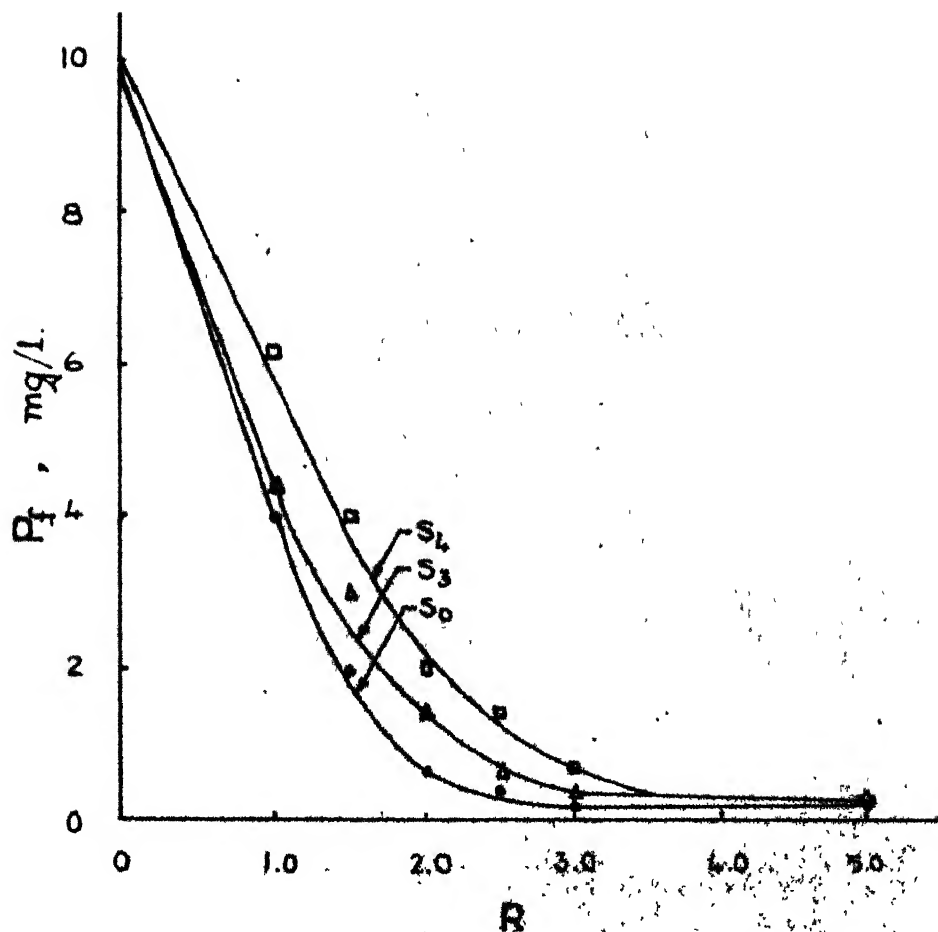
- Pure Phosphate Soln. $P_t = 10$ mg/L. (S_0)
- △- Synthetic Sample $P_t = 10$ mg/L., S.S. = 20 mg/L. (S_1)
- " " $P_t = 10$ mg/L., S.S. = 1000 mg/L. (S_2)

Fig. 9. Effect of Suspended Solid on Phosphate Removal.

4.2.2 EFFECT OF BIO-DEGRADABLE ORGANIC MATTER :

The effect of biodegradable organic matter was studied by conducting the coagulation experiment at FH-6 in synthetic sample prepared by adding peptone in various concentration (125 & 1250 mg/l) to the pure phosphate solution ($P_i = 10$ mg/l). Comparison of the results between pure and synthetic system is shown in fig. 10. It appears that the presence of bio-degradable organic matter of concentration in the range studied does interfere with the alum dose requirement for effective removal of phosphate. The results show that to achieve P_f around 0.5 mg/l (Permissible concentration of Phosphorous in Stream.) dose required is $R = 2.5$ and $R = 3.5$ in case of synthetic sample having peptone concentration 125 mg/l (≈ 20 mg/l B.O.D) and 1250 mg/l (≈ 200 mg/l B.O.D.) respectively.

The combined effects of both suspended solid and bio-degradable organic matter are shown in fig. 11. It is seen that the curve for phosphate removal from IIT/K sewage falls in between those for phosphate removal from two synthetic samples covering the range of B.O.D and suspended solids normally expected in sewage. All the three curves fall above the curve for pure solution of

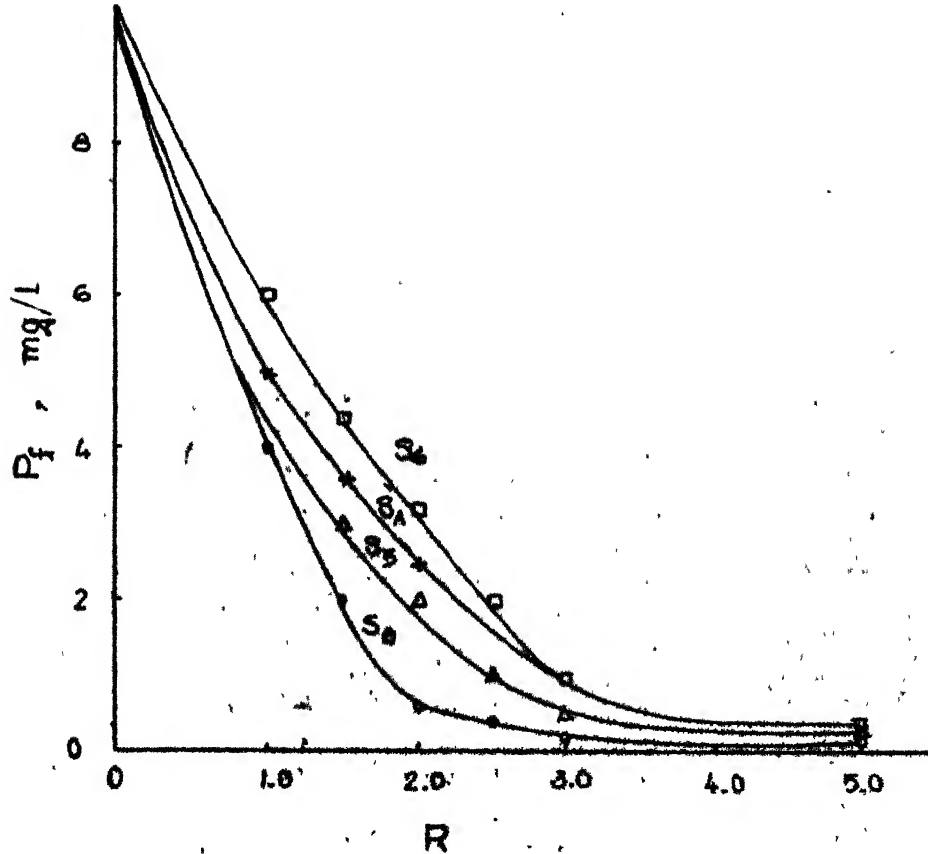


• S_0 : Pure Phosphate Solution, $P_i = 10$ mg/L.

Δ S_1 : Synthetic Sample, $P_i = 10$ mg/L, Pepton = 125 mg/L
(B.O.D. = 30 mg/L)

□ S_2 : Synthetic Sample, $P_i = 10$ mg/L, Pepton = 1250 mg/L
(B.O.D. = 200 mg/L)

Fig. 10. Effect of Biodegradable Organic Matter on Phosphate Removal at pH-6.



- S_0 Pure Phosphate Soln. $P_i = 10 \text{ mg/L}$
- △ S_1 Synthetic Sample $P_i = 10 \text{ mg/L}$, $S.S. = 20 \text{ mg/L}$, $B.O.D. = 20 \text{ mg/L}$
- S_2 " " $P_i = 10 \text{ mg/L}$, $S.S. = 1000 \text{ mg/L}$, $B.O.D. = 200 \text{ mg/L}$
- × S_A Actual Waste Water. $P_i = 10 \text{ mg/L}$
(I.I.T./K Campus raw sewage)

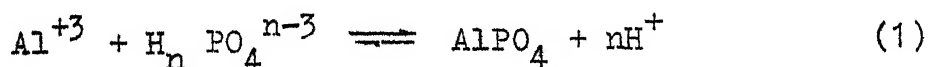
Fig. 11 Comparison of Phosphate removal from Pure Solution, Actual Sewage & Synthetic Waste Samples, PH-6.

same $P_i = 10 \text{ mg/l}$. It is likely that the presence of B.O.D in Sewage reduces efficiency of phosphate removed by alum coagulation.

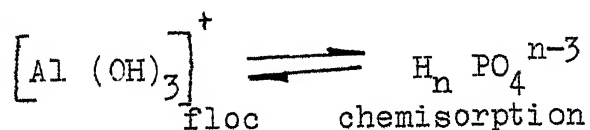
4.3 MECHANISM OF PHOSPHATE REMOVAL FROM AQUEOUS SOLUTION BY ALUM COAGULATION :

It is an established fact that very high degree of phosphate removal (about 95-99%) can be achieved by adding sufficient alum dose. But the actual mechanism of removal is yet to be found out. Two hypothesis have been propounded regarding the mechanism of removal :

- (1) By the straight and simple chemical precipitation of aluminium phosphate.



- (2) By the adsorption of phosphate ions on the positively charged surfaces of aluminium hydroxide flocs.



When alum solution is added to a phosphate solution if only the reaction (1) takes place then we could have achieved almost complete removal of phosphate at Al : P

molar ratio 1:1. But none of the investigators including me found this to be true. In the present work it has been found that at Al:P molar ratio 1:1 the removal is 57-75% (at optimum PH-6.0) depending on initial phosphorous concentration (P_i). On the other hand an alum dose of Al : P molar ratio 2:1 appears to be sufficient for a 95% removal of phosphate. Our possible explanation may be that the precipitate that forms is a mixed hydroxophosphate with an Al : P ratio of 2:1 and a chemical formula something like $Al(OH)_{1.5}(PO_4)_{0.5}$. An attempt was made to determine the nature of the precipitate from its X-ray diffraction pattern. Alum coagulation was carried out at $R = 2.0$, PH = 6, $P_i = 4$ gm/l. The precipitate was filtered out, dried at $100^\circ C$ and examined in an X-ray diffractometer. However, no diffraction peak was obtained suggesting that the freshly precipitated substance is amorphous in nature.

The experiments described so far do not supply any definite conclusion about the second mechanism of phosphate removal i.e. adsorption on $Al(OH)_3$ flocs. Therefore, a new set of experiments were performed in which phosphate solution was added to a freshly prepared aluminium hydroxide suspension. (details in chapter 3). It is assumed

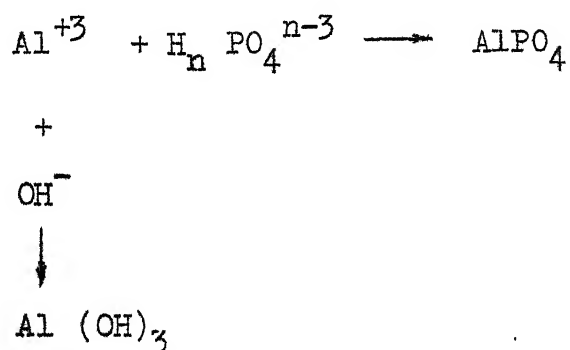
that in these experiments phosphate is removed only by adsorption because the Al is in the solid phase as $\text{Al}(\text{OH})_3$.

4.3.1 COMPARISON BETWEEN TOTAL PRECIPITATION AND ADSORPTION :

Comparison between the results of total precipitation, where alum is added to pure orthophosphate solution and adsorption process, where orthophosphate solution is added to freshly prepared aluminium suspension is shown in fig. 12. One interesting phenomenon was observed in the adsorption process is that when a pure orthophosphate solution of PH-6.5 is added to freshly precipitated aluminium hydroxide colloidal flocs suspension (PH-6.5), PH of the resulting solution gradually increases (although very little : about 0.2). It leads to the conclusion that adsorption of phosphate on the aluminium hydroxide takes place with the replacement of hydroxyl ions. So aluminium hydroxide has got a capacity of removing phosphate by adsorption with a replacement of hydroxyl ions in a chemisorption process. From fig. 12. it is found that extent of removal is different in the two processes. In fact the extent of removal in adsorption process is less than that in total precipitation process.

So at this stage it can be concluded that both chemical precipitation and adsorption phenomena take place simultaneously as a mechanism in the removal of phosphate from aqueous solution by alum coagulation. But this is only a qualitative explanation of the mechanism. To evaluate the removal quantitatively by this mechanism the following should be known :

(1) What percentage of total aluminium added (Al_T) will involve in the chemical precipitation of Al-phosphate. This can be found out if the kinetics of the competitive reaction :



is known, but this was not studied in this work

(2) Capacity of Al^{+3} ion to remove phosphate. Of-course this is already known from the stoichiometric proportion of Al & P in the precipitate $AlPO_4$ and the value is to be $3.52 \text{ gm } PO_4^{-3} / \text{ gm } Al^{+3}$.

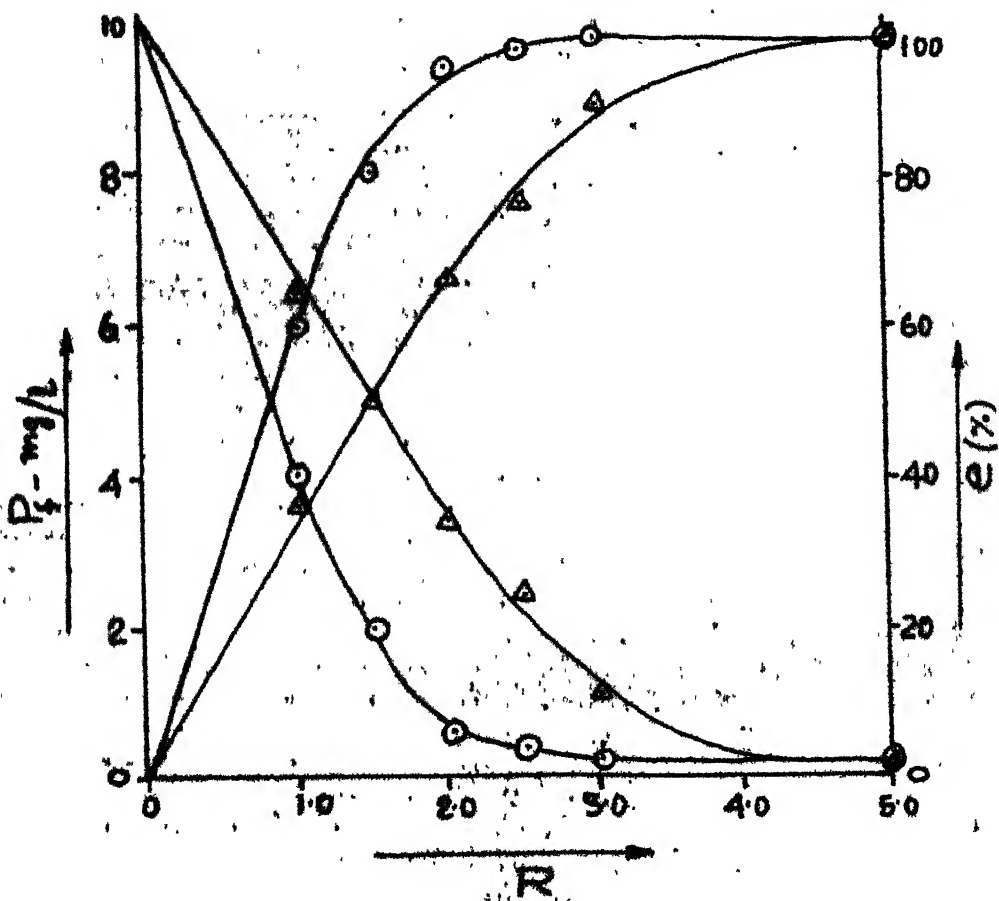
(3) Phosphate adsorbing capacity of $\text{Al}(\text{OH})_3$ flocs which are calculated on the basis of the results obtained by studying the adsorption process separately (results in Table 4).

TABLE - 4

RESULTS OF THE ADSORPTION PROCESS

$P_i = 10 \text{ mg/l}$; PH - around 6.5

R	P_f -mg/l	Removal %	Capacity; mg of PO_4^{3-} /mg of $\text{Al}(\text{OH})_3$
1	6.4	36	0.44
1.5	5.0	50	0.406
2.0	3.4	66	0.403
2.5	2.4	76	0.37
3.0	1.1	8.9	0.362
5.0	0.2	9.8	0.24



▲—▲ ADSORPTION.
 ○—○ TOTAL-PRECIPIATION.

FIG. 12. COMPARISON BETWEEN TOTAL PRECIPITATION AND ADSORPTION. — $P_L = 10 \text{ mg/l}$ AND $\text{PH} \approx 8.0$

From the result it seems that adsorbing capacity depends on residual concentration of phosphate in the effluent.

4.4 RECOMMENDATION :

From the foregoing discussion I would like to recommend that this alum coagulation treatment should be adopted as a tertiary treatment process. To an existing treatment plant this chemical treatment unit could be adopted (i) Before primary clarifier, (ii) Before secondary clarifier or within aeration tank in case of activated sludge plant. These possibilities may eliminate the construction of a further tertiary clarifier resulting a little bit save in capital cost of treatment plant but will involve more cost in other ways due to the reason that dose requirement will be higher than actual because at all these stages the B.O.D concentration will be higher which has a significant effect on dose requirement. Instead if we adopt this chemical treatment as tertiary unit we will have the following beneficial effect :

- (1) Operating cost will be lower than those cases although the capital cost will be increased but in chemical treatment the operating cost is much more importance.

(2) The sludge produced in this chemical treatment (alum coagulation) unit will be more or less pure chemical compounds. And according to Tarrel et-al and lea et al (21) subsequent alum can be recovered from this sludge after digestion. So it is better to handle this sludge separately without intermixing with Primary or Secondary clarifier sludge.

4.4 SUGGESTION OF FUTURE WORK :

- (1) Kinetics study of the competitive reactions taking place in the mechanism of phosphate removal from aqueous solution by alum coagulation.
- (2) Effect of mixing time (both quick & slow) on residual phosphorous concentration in the affluent (P_f).
- (3) Characterisation of sludge produced in the treatment of waste water by alum coagulation of phosphate removal. Characterisation should include (i) Settleability (ii) Water content (iii) Compactability (iv) Dewaterability etc.
- (4) In this study only the orthophosphate has been considered. But in actual case along with orthophosphate there will other dissolved condensed phosphates. So the removal of condensed phosphates by alum coagulation is another aspect of study.

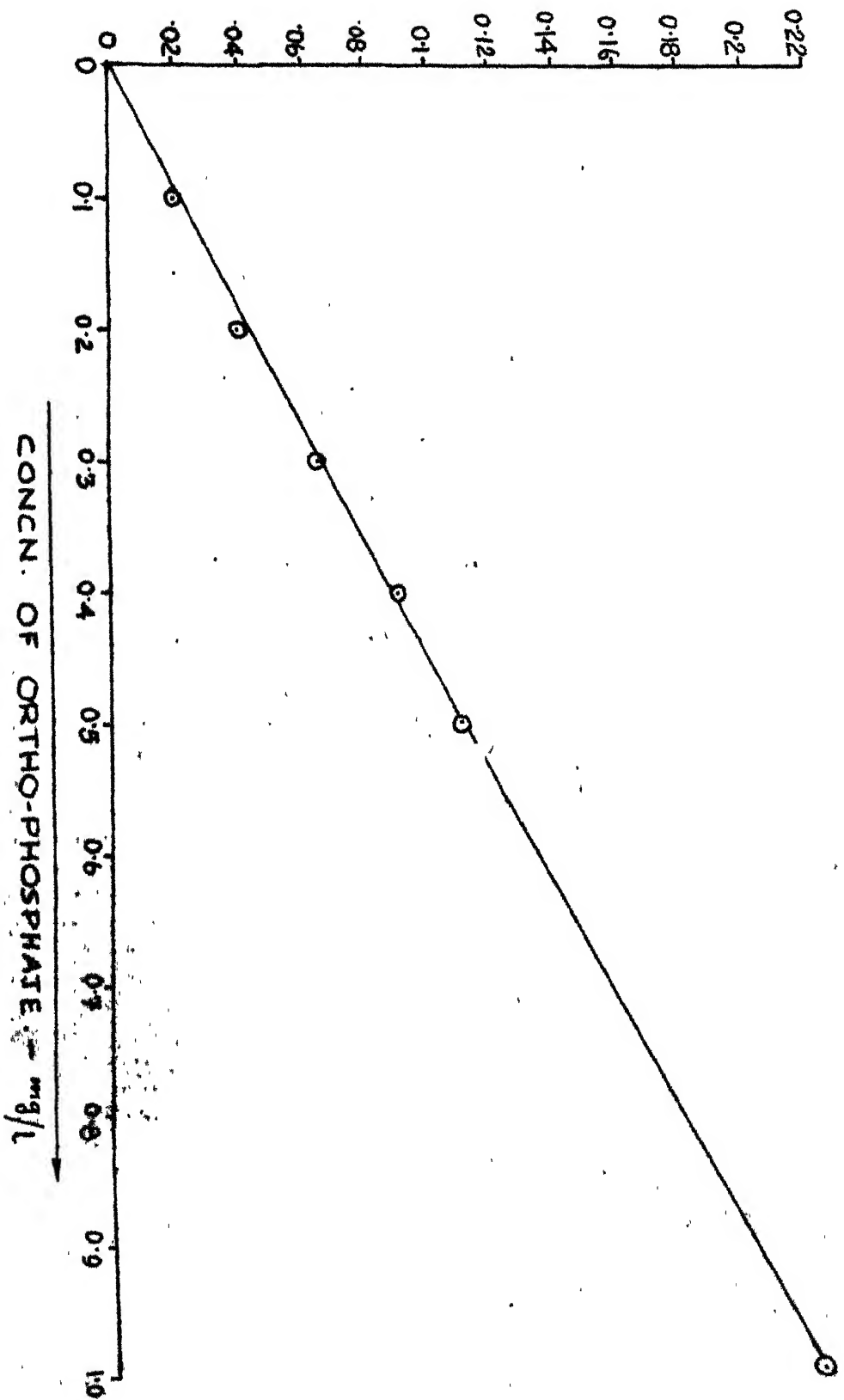


FIG.13. STANDARD CURVE FOR ORTHOPHOSPHATE.

On the basis of the present study the following conclusions can be drawn :

- 1) The optimum PH for maximum removal of phosphorous by alum coagulation is found to be around 6.0.
- 2) The effect of P_i on P_f is significant at $R < 2.0$ but after $R \geq 2.0$ P_f remains constant for a particular R irrespective of P_i .
- 3) The dose requirement at optimum PH - 6 can be suggested Al : P molar ratio 2 : 1 or Alum : P_i weight ratio 7 : 1 for effective removal (to achieve P_f around 0.5 mg/l) of phosphate by alum coagulation in pure system.
- 4) But in actual waste water practice the dose requirement will be more than pure system due to the effect of interfering parameters mainly bio-degradable organic matter.
- 5) The effect of suspended solid is found not so significant.

- 6) Actual increase in dose will depend on the concentration of interfering parameter present in the sample. In synthetic sample having $P_i = 10 \text{ mg/l}$, $S.S = 20 \text{ mg/l}$ and peptone = 125 mg/l (= 20 mg/l B.O.D) which are the usual characteristics of the secondary treatment effluent the increase in dose is found to be 25% of the actual dose required in pure system.
- 7) The algae do not interfere in the removal of phosphate by alum coagulation.
- 8) The mechanism of phosphate removal by alum coagulation is most likely a combination of precipitation, adsorption and ion exchange.
- 9) The nature of the precipitate formed in the coagulation is amorphous even after drying at 100°C .

BIBLIOGRAPHY

1. Adnan Shirdala & Jerry, W. Stewart, "Chemical Coagulation of Effluents from Municipal Waste Stabilization Ponds" - Water & Sewage Works, April 1971 (P-100).
2. Albertson, O.E. and Sherwood, R.J. "Phosphate Extraction Process". Journal WPCF, 1969 (1467).
3. Barth, E.F., and Ettinger, M.B. "Mineral Controlled Phosphorous Removal in the Activated Sludge Process" JWPCF, 1967 (1362).
4. Bache, B.W. - J. Soil Science, 15, 110, (1964).
5. Barth E.F., Jackson B.N., Lewis R.F. and Brenner R.C "Phosphorous removal from Waste Water by Direct Dosing of Aluminate to T.F.", Journal WPCF 1969 (1752).
6. Butler, J.N., Solubility and PH Calculations, Addison-Wesley Publishing Co., Inc.
7. Committee Report, "The Determination of Orthophosphate Hydrolyzable Phosphate and total Phosphate in Surface Waters", Journal ATWA 50 : 1958 (1563).

8. Committee Report, "Chemistry of Nitrogen and Phosphorous in Water". Journal AWWA, Feb. 1970.
9. Don Vacker, C.H. Connell and W.H. Wells - "Phosphate Removal by Activated Sludge at San Antonio, Texas". Chem. Engg. Symp. Series. 78 Vol. 63, 1967 (148) or Journal W.P.C.F. 39, 1967 (750).
10. Davis, S. "Alternatives for Phosphate Removal", Water Sewage Works 117, 1970 (336).
11. Dickeason, E.W., and Farrell P.V., "Laboratory and Pilot Plant Studies on Phosphate Removal from Industrial Wastes". Journal WPCF 56, 1969.
12. Eberhardt, W.A., and Nesbutt, J.B., "Chemical Precipitation of Phosphorous in a High Rate Activated Sludge System", Journal W.P.C.F. 1968 (1239).
13. Eliassen, R "Removal of Nitrogen and Phosphorous" Published in 23rd Industrial Waste Conference 1968, Purdu University.
14. Fruh, E.G., Stewart, K.A., Lee, G.E. and Rolich, G.A. "Measurement of Entrophication and Trends", Journal W.P.C.F. Vol. 38. Aug. 1966 (1237).

- 15a. Gilbert. V. Levin and Joseph Shapiro, "Metabolic Uptake Of Phosphorous by Waste Water Organisia" Journal W.P.C.F. 1965 (800).
16. Hall M.W. and Engelbrrrecht R.S. "Phosphorous removal Past, Present, Future" Water and Waste Engg. 1969.
17. Horn J.A., De Prater B.L. and Witherrow J.L. "Phosphate Removal at Fort Worth Texas". Water and Waste Engg. 1969.
18. Irving, Yall et-al. "Phosphorous Utilization by Microorganisms of Activated Sludge", Chem. Engg. Sym Seria. 78, Vol. 63, 1967 (148).
19. Kittrick, J.A and Jackson M.L., 'Journal Soil Science 1964, (110).
20. Lawrence A. Schmied, Ross, E. Mexiurey, "Phosphate Removal by Lime Biological Treatment Scheme" - Journal W.P.C.F. July 1969 (1259).
21. Lea, W.G., Rolich, S.A. and Katz, W.J. - Sewage and Industrial Waste, 26, 201, 1954.
22. Mackenthum, X.M."The Phosphorous Problem". Journal AWWA 1968 (1047).
23. Missingham G.A. "Occurence of Phosphate in Surface Water and Some Related Problems" JAWWA, 1967 (183).
- 15*. Ghassemi, M., and Recht, E.L."Kinetics of Phosphate Precipitation Using Alum & Ferric Salts" - ACS Divn. Of Water, Air and Waste Chem. Reprints.10,1.1 (1970)

24. Milton Spiegel and Tom. H. Forrest. "Phosphate removal - Summation of Papers". Journal Sanitary Engg. Division A.S.C.E. Vol. 95, Oct. 1969.
25. Milbury, W.F. et-al "Effects of D.O. on Phosphorous Removal in Municipal Activated Sludge Treatment" Chemical Engg. Sym. Series 107, Vol. 67 1971 (100).
26. Morris E. Gales. Jr. Eleno, C. Julian and Robert, C. Krouer - "Method for Quantitative Determination Of Phosphorous", Journal AWWA 58, 1966 (1363).
27. Muljate, D.; Posner, A.M. and Quirk, J.P. - Journal Soil Sc. 17, 1966 (212).
28. Nesbitt, J.B "Phosphorous Removal, The State of the Art", Journal WCTF, Vol. 41, May 1969 (701).
29. Owen R. "Removal of Phosphorous from Sewage Plant Effluent with Time" - Journal Sewage and Industrial Waste May 1953.
30. Popel, J "Phosphorous Removal with Ferric iron and Aluminium" Advances in Water Pollution Research 1969 (643).
31. Ronald, G. Schuessler "Phosphorous Removal : A Controllable Process" Water - 1970, Chem. Engg. Symp. Series 107, Vol. 67, 1971, (536). A.I.C.E.

32. Robert, L. Bunch, "Factors Influencing Phosphorous Removal by Biological Treatment" Chem. Engg. Sym. Series (A.I.Ch.E) 107, Vol. 67 1971 (90).
33. Robert, D. Barman et-al "Continuing Studies in the Removal of Phosphorous by Activated Sludge Process" - Chem. Engg. Symp. Series (AI Ch.E), 107, Vol. 67, 1971 (117).
34. Rolich, G.A. "Methods for Removal of Phosphorous and Nitrogen From Sewage Plant Effluent" - Advances in Water Pollution Research Vol. 2 (207).
35. Ryther, J.H. and Dunstan Wal - "Nitrogen Phosphorous and Eutrophication in the Coastal Marine Environment" Science, 12 March, 1971 (1008).
36. Sawyer, C.N "Some New Aspects of Phosphates in Relation to Lake Fertilization", Journal, Sewage and Industrial Waste 24,6, June 1952 (768).
37. Sawyer, C N "Chemistry for Sanitary Engineers", McGraw Hill Book Company, Inc.
38. Sawyer, C.N "Basic Concepts of Eutrophication" Journal WPCF, vol. 38, No.5, May 1966 (737).
39. Siddiqui, R.H., Sehgal, J.R. and Sachan P.C.- "Characteristics of Waste Water" Part-I Report of CSIR Research Scheme No. 18(2)/67-GAU-11, Dept. of Civil Engg., IIT/K, U.P. (1969).

40. Sletten, O & Bach, C.H. "Modified Stannous Chloride Reagent for Orthophosphate Determination" Journal AWWA 53, 1961 (1031).
41. Stumm, W and Morgan J.J.- "Chemical Aspects of Coagulation" - Journal AWWA, 54, 1962 (971).
- **
42. Stumm, W.- "Discussion" Advance in Water Pollution Research Vol. 2 (216). The Macmillan Company.
43. Sanning, D.E. "Phosphorous Determination - A Method Evaluation Journal, Water Sewage Works 1967(131).
44. Sawyer C N "The Need of Nutrient Control". Journal WACP 1968, (363).
45. Sastry. C A "Removal of Phosphorous from Sewage by Different Methods" Environ. Health, 1965 (213)
46. Sreenivasan, A. - "Eutrophication Trends in a Chains of Artificial Lakes in Madras (India)" Env. Health, Vol. 11, Oct. 1969 (392).
47. Scalf, H.P. - "Phosphate Removal at Baltimore, Manford" Journal, Sanitary Engg. Division, ASCE, Vol. 95, Oct. 1969.
48. Steven, G. Jarkovic, Dec, T. Mitchell and James, C. Buzel Jr. "Measurement of Phosphorous in Waste Water". Water Sewage Works, 1967 (471).

** 41a Stumm. W. and Morgan. J.J. "Aquatic Chemistry", Wiley Interscience Inc. (1970).

49. Standard Method for the Examination of Water and Waste Water, 12th Edition, APHA.
50. Tekippe R.J. and Han P.K. - "Coagulation Testing, A Comparision of Techniques - 'Part I & II". Journal AWWA. Vol. 62, 1970 (554 & 620).
51. Thomas, E. Bailey - "Measurement and Detection of Entrophication" Journal Sanitary Engg. Division ASCE 93, 1967, (121).
52. Weiss, C - "Relation of Phosphate to Entrophication" Journal A.W.W.A. 1969 (337).
53. Waldichuck, W. "Entrophication Studies in a Shallow Inlet in Vancouner Island" Journal W.P.L.F. 1969 (745).

APPENDIX - A

EXPERIMENTAL DATA FOUND IN LABORATORY

Values of P_f - mg/l at different PH and R

TABLE - 1a

Pure System : $P_i = 30 \text{ mg/l}$

PH	4.0	5.0	6.0	7.0	8.0	9.0
R (R')						
1.0 (3.5)	19.8	7.5	7.0	8.0	21.2	22.0
2.0 (7.0)	2.4	0.8	0.6	1.04	2.5	19.8
3.0 (10.5)	1.6	0.33	0.16	0.4	0.8	18.8

TABLE - 1b

Pure System : $P_i = 10 \text{ mg/l}$

PH	4.0	5.0	6.0	7.0	8.0	9.0
R (R')						
1.0 (3.5)	8.4	4.3	4.0	4.4	8.0	9.5
2.0 (7.0)	2.5	1.7	0.6	1.8	2.8	9.0
3.0 (10.5)	2.0	0.5	0.2	0.6	0.7	9.0

TABLE - 1c

Actual System : $P_i = 10.5 + 0.5 \text{ mg/l}$

(IIT/K Campus raw sewage)

	<u>PH</u>					
$R (R')$	4.0	5.0	6.0	7.0	8.0	9.0
1.0 (3.5)	8.4	5.8	5.0	7.5	8.4	-
2.0 (7.0)	3.6	2.65	2.5	4.0	6.2	-
3.0 (10.5)	2.8	2.0	1.0	2.2	4.4	-

TABLE - 2

Values of P_f -mg/l at PH - 6 at different P_i & R
in Pure System

	<u>R(R')</u>					
P_i (mg/l)	1.0 (3.5)	1.5 (5.25)	2.0 (7.0)	2.5 (8.75)	3.0 (10.5)	5.0 (17.5)
4.0	1.7	1.0	0.5	0.4	0.2	0.2
10.0	4.0	2.0	0.6	0.4	0.2	0.16
20.0	6.4	3.0	0.8	0.5	0.28	0.2
30.0	7.0	3.4	0.6	0.24	0.16	0.16

TABLE - 4

Values of P_f - mg/l at PH-6 at different R in Synthetic
System ($P_i = 10.0$ mg/l)

R (R')	1.0	1.5	2.0	2.5	3.0	5.0
Synth etic Samples	(3.5)	(5.25)	(7.0)	(8.75)	(10.5)	(17.5)
$S_1: P_i = 10$ mg/l S.S = 20 mg/l	3.0	1.4	0.52	0.32	0.28	0.28
$S_2: P_i = 10$ mg/l S.S=1000 mg/l	4.0	1.2	0.8	0.6	0.2	-
$S_3: P_i = 10$ mg/l BOD=20 mg/l	4.4	3.0	1.4	0.6	0.4	0.3
$S_4: P_i = 10$ mg/l BOD=200 mg/l	6.2	4.0	2.0	1.48	0.64	0.28
$S_5: P_i = 10$ mg/l S.S=20 mg/l BOD=20 mg/l	4.0	3.0	2.0	1.0	0.5	0.3
$S_6: P_i = 10$ mg/l S.S=1000 mg/l BOD = 200 mg/l	6.0	4.4	3.2	2.0	1.0	0.4

TABLE - 3

Values of P_f - mg/l at PH-6, at different P_i & R in actual system

R (R') →	1.0	1.5	2.0	2.5	3.0	5.0
P_i (mg/l)	(3.5)	(5.25)	(7.0)	(8.75)	(10.5)	(17.5)
SEWAGE	5.0	3.6	2.5	2.0	1.0	0.3
10.0±0.5						
OXIDATION POND EFFLUENT	1.56	0.8	0.52	0.4	0.15	0.15
3.5±0.5						

TABLE - 5

Results of the separate adsorption process in pure system

$P_i = 10$ mg/l , PH - around 6.5

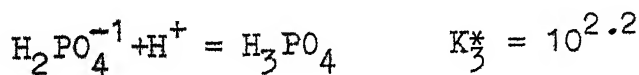
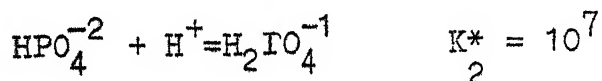
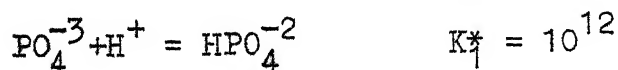
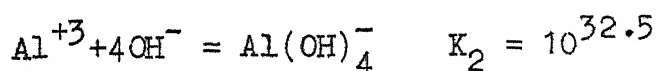
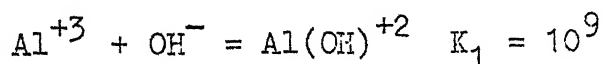
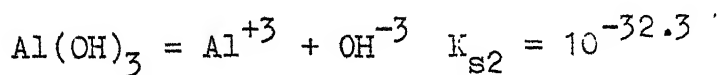
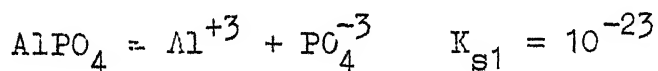
R (R')	1.0	1.5	2.0	2.5	3.0	5.0
	(3.5)	(5.25)	(7.0)	(8.75)	(10.5)	(17.5)
P_f (mg/l)	6.4	5.0	3.4	2.4	1.1	0.2

APPENDIX - B

CALCULATION OF SOLUBILITY DATA OF AlPO_4 & $\text{Al}(\text{OH})_3$ AS A FUNCTION OF PH ON THE BASIS OF AVAILABLE THERMOCHEMICAL

DATA

Equilibrium constants of the following reaction are taken from stumm & Morgan (11a)



Now
$$\text{Al}_T = [\text{Al}^{+3}] + [\text{Al}(\text{OH})^{+2}] + [\text{Al}(\text{OH})_4^{-1}]$$

$$\text{P}_T = [\text{PO}_4^{-3}] + [\text{HPO}_4^{-2}] + [\text{H}_2\text{PO}_4^{-1}] + [\text{H}_3\text{PO}_4]$$

where : Al_T = Total dissolved aluminium species.

P_T = Total dissolved orthophosphate species.

Fraction of Al^{+3} species, $\alpha_{\text{Al}} = \frac{[\text{Al}^{+3}]}{\text{Al}_T}$

$$= \frac{1}{1 + \frac{K_1 \times 10^{-14}}{[\text{H}^+]} + \frac{K_2 \times 10^{-56}}{[\text{H}^+]^4}}$$

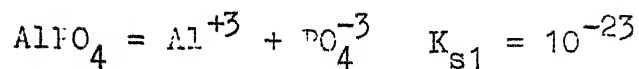
Fraction of PO_4^{-3} specie, $\alpha_p = \frac{[\text{PO}_4^{-3}]}{P_T}$

$$= \frac{1}{1 + K_1^* [\text{H}^+] + K_1^* K_2^* [\text{H}^+]^2 + K_1^* K_2^* K_3^* [\text{H}^+]^3}$$

PH	4	5	6	7	8	9	10	11	12	13
$-\log \alpha_{\text{Al}}$	0.041	0.3	1.695	4.5	8.5	12.5	16.5	20.5	24.5	28.5
$-\log \alpha_p$	10.068	9.068	7.042	5.3	4.042	3.005	2.005	1.045	0.3	0.04

Solubility of AlPO_4 & $\text{Al}(\text{OH})_3$:

Case I : When only AlPO_4 is formed.



$$\therefore K_{s1} = [\text{Al}^{+3}] [\text{PO}_4^{-3}]$$

$$\text{Again } [\text{Al}^{+3}] = \alpha_{\text{Al}} \text{ Al}_T \quad \& \quad [\text{PO}_4^{-3}] = \alpha_p \text{ P}_T$$

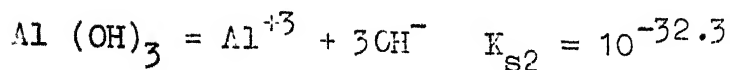
$$\text{Therefore, } \text{Al}_T \cdot \text{P}_T = \frac{K_{s1}}{\alpha_{\text{Al}} \alpha_p} \quad (1)$$

$$\text{and } \text{Al}_T = \text{P}_T \quad (2)$$

From equation (1) and (2)

PH	4	5	6	7	8	9	10	11
-log Al_T or -log P_T	6.441	6.816	7.131	6.6	5.227	3.747	2.247	.727

Case 2 : When only Amorphous $Al(OH)_3$ is formed.



$$\therefore K_{s2} = [Al^{+3}] [OH^-]^3$$

$$\text{Again, } [Al^{+3}] = \alpha_{Al} \cdot Al_T$$

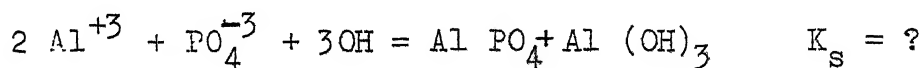
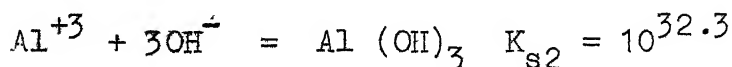
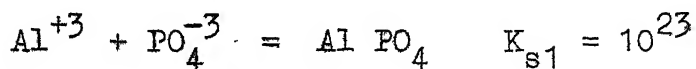
$$\text{Therefore, } Al_T = \frac{K_{s2}}{\alpha_{Al} [OH^-]^3}$$

$$\text{or } \log Al_T = \log K_{s2} - \log \alpha_{Al} + 42 - 3 PH$$

PH	4	5	6	7	8	9	10	11
----	---	---	---	---	---	---	----	----

$-\log Al_T$	2.259	5.00	6.605	6.8	5.8	4.8	3.8	2.8
--------------	-------	------	-------	-----	-----	-----	-----	-----

Case 3 : When both $AlPO_4$ & $Al(OH)_3$ are formed



$$\begin{aligned}
 K_s &= \frac{1}{[Al^{+3}]^2 [PO_4^{-3}] [OH^-]^3} \\
 &= \frac{1}{[Al^{+3}] [PO_4^{-3}]} \cdot \frac{1}{[Al^{+3}] [OH^-]^3} \\
 &= K_{s1} \cdot K_{s2} = 10^{55.3}
 \end{aligned}$$

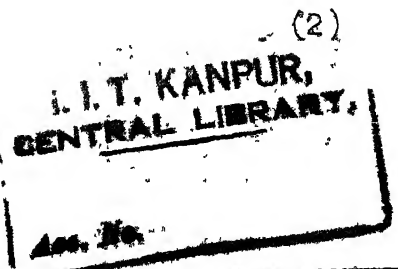
Again $[Al^{+3}] = \alpha_{Al} \cdot Al_T$ and $[PO_4^{-3}] = \alpha_p \cdot P_T$

Putting the values of $[Al^{+3}]$ and $[PO_4^{-3}]$ in above equation

$$Al_T^2 \cdot P_T = \frac{[H^+]^3 \cdot 10^{-13.3}}{\alpha_{Al}^2 \alpha_p} \quad (1)$$

and, $Al_T = 2P_T$ (2)

Solving equation 1 and 2, we get



PH	4	5	6	7	8	9	10	11.
$-\log P_T$	5.251	6.412	7.157	6.874	5.621	4.301	2.966	1.620
$-\log Al_T$	4.951	6.112	6.857	6.574	5.321	4.001	2.666	1.320